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Research Article

Artificial core-shell cofired architectures for high-performance microwave dielectric ceramics

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Abstract: The rapid advancement of 5G/6G communication technologies imposes ever-increasing demands on microwave dielectric ceramics (MWDCs). However, it remains challenging to simultaneously achieve good temperature stability and high $Q \times f$ values. Metamaterials with artificially designed structures exhibit extraordinary properties, and metamaterialogy holds great potential for advancing conventional materials. Inspired by this paradigm, an artificial core-shell cofired architecture was designed to realize high-performance MWDCs. The architecture employed the $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ (ZNO) matrix as the shell and positive- τ_f compensators, including TiO_2 (TO), CaTiO_3 (CTO), or SrTiO_3 (STO), in either green or pre-sintered states, as cores. The τ_f values of all the core-shell samples were effectively tuned to near zero while high $Q \times f$ values were retained. Specifically, the ZNO-TO core-shell ceramic with a 1.43 wt% pre-sintered TO core exhibited $\epsilon_r \sim 25.32$, $Q \times f \sim 119,100$ GHz, and $\tau_f \sim -4.8$ ppm/ $^{\circ}\text{C}$, while the temperature-stable counterparts using the CTO or STO cores retained $Q \times f \geq 67,800$ GHz. Furthermore, HFSS simulation of a cylindrical dielectric resonator antenna (CDRA) based on the optimized ZNO-TO core-shell ceramic predicted favorable impedance matching (VSWR ~ 1.015), radiation efficiency above 90%, and a peak realized gain of 6.13 dBi at 4.31 GHz. It preliminarily demonstrates the feasibility of CDRA applications. The artificial core-shell architecture provides a general strategy for synergistically optimizing microwave dielectric properties by tailoring the electric-field participation and confining heterogeneous interfacial reactions, which is beneficial to developing high-performance MWDCs required for next-generation communication technologies.

Keywords: microwave dielectric ceramics (MWDCs), artificial core-shell architecture, temperature stability, low dielectric loss, ZnNb_2O_6 .

1 Introduction

The rapid advancement of wireless communication technologies, including 5G/6G, the Internet of Things, and autonomous driving, requires microwave devices that combine high-frequency operation, temperature stability, low loss, and miniaturization [1-3]. Microwave dielectric ceramics (MWDCs) are key materials for resonators, filters, and antennas and play a critical role in determining the device efficiency, bandwidth, and stability [4]. Therefore, MWDCs are required to possess a near-zero temperature coefficient of resonant frequency (τ_f) and low dielectric loss (high $Q \times f$; $Q = 1/\tan\delta$). However, achieving a near-zero τ_f without sacrificing $Q \times f$ values remains a key challenge.

Numerous efforts have been devoted to tuning the τ_f of MWDCs. As summarized in Fig. 1, these approaches can be divided into conventional material modification strategies and artificially structured material strategies [5-15]. Conventional approaches include composite formation using constituents with opposite τ_f values, such as the K20-series (MgO-TiO₂)-CaTiO₃ ceramics [5,16-18], and host lattice modification through ionic substitution. The latter includes (i) solid-solution formation, such as the typical K45-series, CaTiO₃-LnAlO₃ ($Ln = \text{La, Nd}$) [6]; (ii) oxygen octahedral tilting in complex perovskites, such as $A(B'_{1/3}B''_{2/3})\text{O}_3$ ($A = \text{Ba, Sr}$; $B' = \text{Mg, Zn}$; $B'' = \text{Ta, Nb}$) and Ba₂Ca_{1-x}Sr_xWO₆ [7,19]; and (iii) the rattling effect caused by small ions entering the A site, as in Bi_{1-x}Ho_xVO₄ ceramics [8]. Although these strategies are effective, they modify the composition or crystal structure throughout the material. When the modification exceeds the host's tolerance, unexpected secondary phases and additional dielectric loss may result during high-temperature sintering.

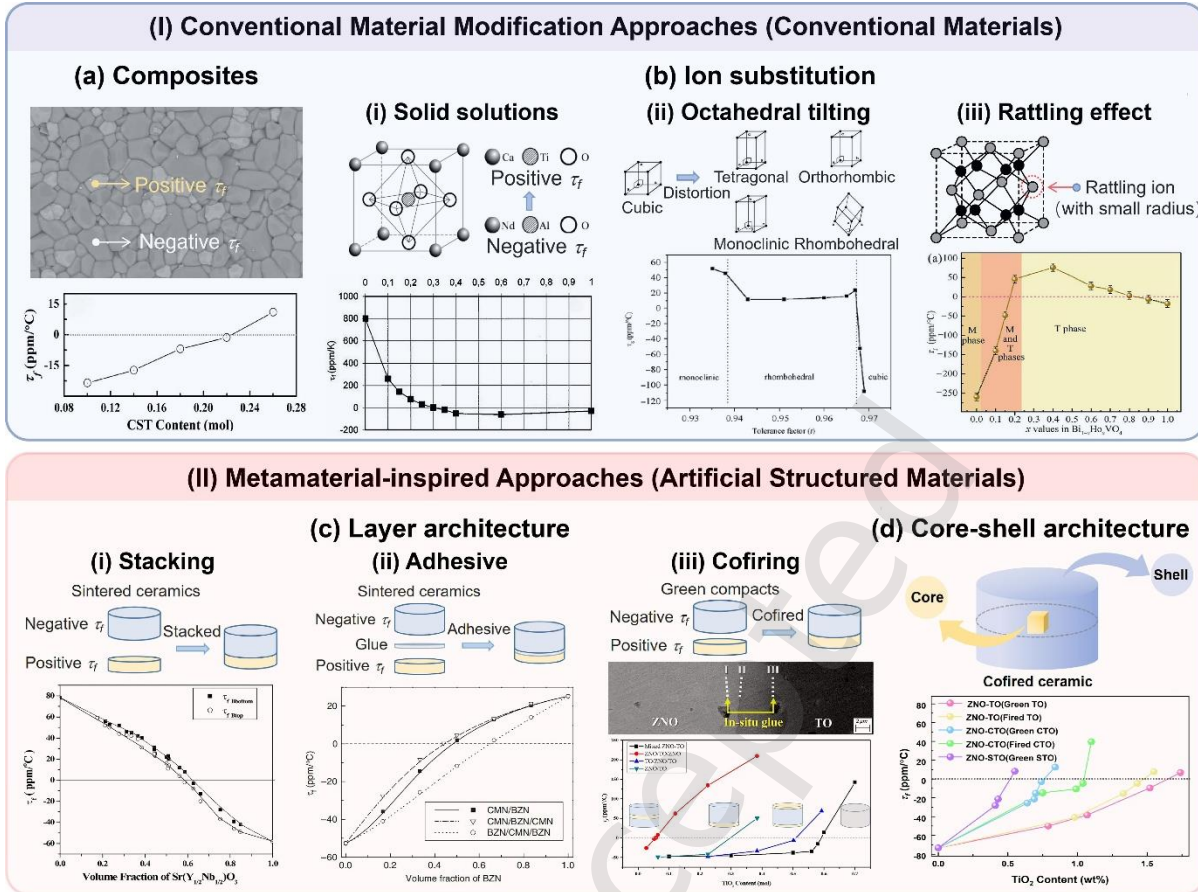


Fig. 1 Strategies for tuning τ_f toward zero in MWDCs. Conventional material modification approaches: (a) composites, such as $(\text{MgO-TiO}_2)\text{-Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ceramics, reproduced from Ref. [5]; (b) ionic substitution, including (i) solid solutions, such as $(1-x)\text{CaTiO}_3\text{-}x\text{NdAlO}_3$ ceramics, reproduced from Ref. [6], (ii) oxygen octahedral tilting, such as $\text{Ba}_2\text{Ca}_{1-x}\text{Sr}_x\text{WO}_6$ ceramics, reproduced from Ref. [7], and (iii) the rattling effect, such as $\text{Bi}_{1-x}\text{Ho}_x\text{VO}_4$ ceramics, reproduced from Ref. [8]. Artificial structured material approaches: (c) layered architecture, including (i) stacking, such as $\text{Ba}_5\text{Nb}_4\text{O}_{15}\text{-Sr}(\text{Y}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics, reproduced from Ref. [9], (ii) adhesive bonding, such as $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics, reproduced from Ref. [10], and (iii) cofiring, such as $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-TiO}_2$ ceramics, reproduced from Ref. [11]; and (d) the core-shell cofired architecture developed in this work.

Metamaterials with artificially designed structures exhibit extraordinary properties beyond those of conventional materials. This paradigm, referred to as metamaterialogy, offers opportunities for advancing conventional materials, and the multilayer ceramic capacitor (MLCC) and low-temperature cofired ceramic (LTCC) technologies align squarely with its structural design principles [20]. Recently,

increasing attention has been paid to regulating material properties through artificial structural architectures, providing new opportunities for overcoming the performance limitations of traditional materials. Following this concept, layered dielectric resonators fabricated by stacking, bonding, or cofiring MWDCs with opposite τ_f signs represent a typical metamaterial-inspired approach [21-27]. Near-zero τ_f has been achieved in various artificial structured material systems, including stacked resonators [Ba₅Nb₄O₁₅-Sr(Y_{1/2}Nb_{1/2})O₃, MgTiO₃-CaTiO₃] [9,23], adhesive-bonded multilayer resonators [Ca(Mg_{1/3}Nb_{2/3})O₃-Ba(Zn_{1/3}Nb_{2/3})O₃, Ba₂Ti₉O₂₀-Ba_{1.85}Sm_{4.1}Ti₉O₂₄] [10,24], and layered cofired resonators (Zn_{1.01}Nb₂O₆/TiO₂/Zn_{1.01}Nb₂O₆, Mg₄Nb₂O₉/TiO₂/Mg₄Nb₂O₉, and MgTiO₃/TiO₂/MgTiO₃) [11,26,27]. Actually, organic adhesives are susceptible to aging, leading to structural degradation and dielectric performance deterioration, while layered cofired architectures achieve both good temperature stability and high $Q \times f$ values by forming in-situ bonded interfaces. Nevertheless, it is challenging to achieve well-bonded configurations of layer cofired ceramics in the case of obvious mismatch in sintering shrinkage between heterogeneous layers. More recently, a core-shell architecture was designed in the low-permittivity MFL_{0.5}-TiO₂ system by embedding a pre-densified TiO₂ core within a continuous MFL_{0.5} shell, showing good regulation of microwave dielectric response [28].

To further leverage the advantages of metamaterial-inspired design while overcoming the limitations of layered architectures, we systematically extended this novel strategy using an artificial core-shell cofired architecture to achieve near-zero τ_f while retaining high $Q \times f$ values. Zn_{1.01}Nb₂O₆ (ZNO) was selected as the shell material because of its high $Q \times f$ value ($\sim 83,700$ GHz), moderate ϵ_r (~ 25), and negative τ_f value (-56 ppm/ $^{\circ}$ C) [29,30]. These favorable properties originate from its stable and highly symmetrical crystal structure, which consists of a three-dimensional crystal framework of [ZnO₆] and [NbO₆] octahedra with an ordering sequence of Zn-Nb-Nb-Zn-Nb-Nb along the a -axis [31]. Moreover, Belous *et al.* [32] reported that tuning the Zn/Nb ratio can enhance the $Q \times f$ values of ZnNb₂O₆ by reducing the porosity of the sintered ceramics. Notably, at the specific composition of

$\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$, the $Q \times f$ value can reach 120,000 GHz [32], indicating extremely low dielectric loss. Meanwhile, the negative τ_f of $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ needs to be compensated by adding a component that exhibits a large positive τ_f . Rutile TiO_2 ($\tau_f \approx +450$ ppm/ $^\circ\text{C}$) [33-35], perovskite-type CaTiO_3 ($\tau_f \approx +900$ ppm/ $^\circ\text{C}$) [36], and SrTiO_3 ($\tau_f \approx +1200$ ppm/ $^\circ\text{C}$) [37] were therefore selected as compact positive τ_f cores [38-41].

In this work, a series of artificial core-shell cofired ceramics, $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-TiO}_2$ (ZNO-TO), $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-CaTiO}_3$ (ZNO-CTO), and $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-SrTiO}_3$ (ZNO-STO), were fabricated. The microstructures, phase composition, and microwave dielectric properties were systematically investigated. Furthermore, the HFSS eigenmode solver was employed to simulate the $Q \times f$ values and electric field distribution of the ZNO-TO core-shell ceramics. The agreement between the simulated and experimental trends further validated the feasibility of the artificial core-shell architecture strategy. To explore additional potential for device applications, a cylindrical dielectric resonator antenna (CDRA) based on the optimized ZNO-TO core-shell ceramics was designed and simulated.

2 Experimental

A series of artificial core-shell ceramics, namely $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-TiO}_2$ (ZNO-TO), $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-CaTiO}_3$ (ZNO-CTO), and $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6\text{-SrTiO}_3$ (ZNO-STO), were fabricated via a cofiring process. The constituent ZNO, TO, CTO, and STO ceramics were first synthesized separately by the conventional solid-state route. High-purity raw materials (99.99%, Aladdin), including ZnO , Nb_2O_5 , TiO_2 , CaCO_3 , and SrCO_3 , were weighed in stoichiometric proportions. Each mixture was ball-milled at 300 rpm for 4 h, dried, sieved, and calcined. As ZNO calcined at 1000 $^\circ\text{C}$ usually has an optimum sintering temperature near 1200 $^\circ\text{C}$, TO powder was pretreated at 1050 $^\circ\text{C}$ for 4 h to improve cofiring compatibility, whereas CTO and STO were calcined at 1150 $^\circ\text{C}$. The calcined powders were remilled, dried, sieved, mixed with 5 wt% PVA binder, and sieved again before pressing.

The preparation procedure is shown in Fig. S1. Green TO, CTO, and STO powders were uniaxially pressed at 200 MPa into blocks of varying dimensions. For each core-shell sample, one-half of the

designed ZNO shell mass was first uniaxially pressed to form the bottom shell layer. The core block was then placed at the geometric center, with its central axis aligned with the cylindrical axis, before the remaining one-half of the ZNO powder was added and pressed to form the upper shell layer. The resulting cylinder had a diameter of 10 mm and a thickness of 5-6 mm. Green-core contents were 0.79-1.74 wt% TO, 0.64-0.84 wt% CTO, and 0.41-0.55 wt% STO, respectively. Pre-sintered cores were prepared at 1250-1300 °C, machined into blocks, and assembled in the same manner; their contents were 0.90-1.55 wt% TO, 0.75-1.10 wt% CTO, and 0.31-0.96 wt% STO, respectively. Available dimensions for the pre-sintered TO and CTO blocks are selected and listed in Table S1. After PVA burnout at 600 °C for 4 h, all samples were cofired at 1200 °C for 4 h. After cofiring, the core retained a rectangular block-like shape (Fig. S2), with no substantial deformation or shape distortion observed in the core-shell cofired ceramic architecture.

The phase compositions and crystal structures of the as-prepared powders and ceramics were characterized by X-ray diffraction (XRD, SmartLab, Rigaku, Japan). To characterize the core-shell interfaces, the microstructures and elemental distributions were examined using a field-emission scanning electron microscope (FE-SEM, Zeiss Sigma 360, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS). The microwave dielectric properties (ϵ_r , $Q \times f$, and τ_f) were measured using the Hakki-Coleman method [42] with a network analyzer (HP8720ES, Hewlett-Packard, USA) and a temperature chamber (MC-811T, Espec, Japan). The τ_f values were calculated using Eq. (1):

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \quad (1)$$

where f_0 and f_T are the resonant frequencies measured at T_0 (25 °C) and T (80 °C), respectively. The resonant frequency, $Q \times f$ value, and electric-field distribution of the ZNO-TO core-shell cofired ceramics within the cavity were simulated with the HFSS eigenmode solver based on the measured cavity and sample dimensions.

3 Results and discussion

3.1 ZNO-TO core-shell cofired ceramics

3.1.1 Crystal structure

The XRD patterns of the shell and core samples are shown in Figs. S3 and S4. Both the sintered $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramics (1200 °C, 4 h) and the calcined powders (1000 °C, 4 h) exhibit a pure columbite phase (ZnNb_2O_6 , PDF#00-037-1371) without detectable secondary phases. The XRD profiles of the sintered TiO_2 ceramics (1250 °C, 4 h) and the calcined TiO_2 powders (1050 °C, 4 h) are indexed to a single rutile structure (PDF#00-021-1276). The overall phase compositions of representative ZNO-TO core-shell cofired ceramics are shown in Fig. S5. Only columbite ZnNb_2O_6 and rutile TiO_2 peaks are detected, with no additional reflections assignable to an appreciable crystalline reaction phase.

For comparison, Zhang *et al.* [33] reported composition-dependent phase evolution in conventionally mixed $(1-x)\text{Zn}_{1.01}\text{Nb}_2\text{O}_6-x\text{TiO}_2$ ceramics. The ordered columbite solid solution persisted at $0 \leq x \leq 0.3$; an ixiolite $\text{ZnTiNb}_2\text{O}_8$ phase formed at $0.50 \leq x \leq 0.56$; ixiolite coexisted with rutile $(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.5}\text{Ti}_{0.5}\text{O}_2$ at $0.58 \leq x \leq 0.60$; and a nearly single rutile phase occurred at $x = 0.70$. The total TO contents used here (0.79-1.74 wt%) correspond to $x \approx 0.034$ -0.072 under the assumption of homogeneous mixing and therefore fall within the reported columbite solid-solution region. The observations indicate limited interdiffusion and possible local solid-solution formation rather than a detectable bulk secondary reaction phase at the heterogeneous ZNO/TO interfaces.

3.1.2 Microstructure

The surface SEM image of the pure $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramics sintered at 1200 °C is shown in Fig. S6, from which a dense microstructure with uniformly distributed rod-shaped grains can be observed. The EDS elemental mapping reveals homogeneous distributions of Zn, Nb, and O, which is consistent with the single-phase composition confirmed by the XRD results discussed above. Backscattered electron (BSE) imaging was employed to examine the compositional distribution of the ceramic materials, revealing distinct phases through grayscale contrast variations. Figure 2 presents cross-sectional BSE

images and EDS line scans of ZNO-TO core-shell ceramics with green and fired TO cores, and an SEM image of the cross-section $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ - TiO_2 interface cofired with a green TiO_2 core is shown in Fig. S7 for comparison. The darker region is TO and the brighter region is ZNO. A compositionally graded zone is visible at the interfaces, indicating a limited interdiffusion region with possible local solid-solution formation as discussed above (Fig. S5).

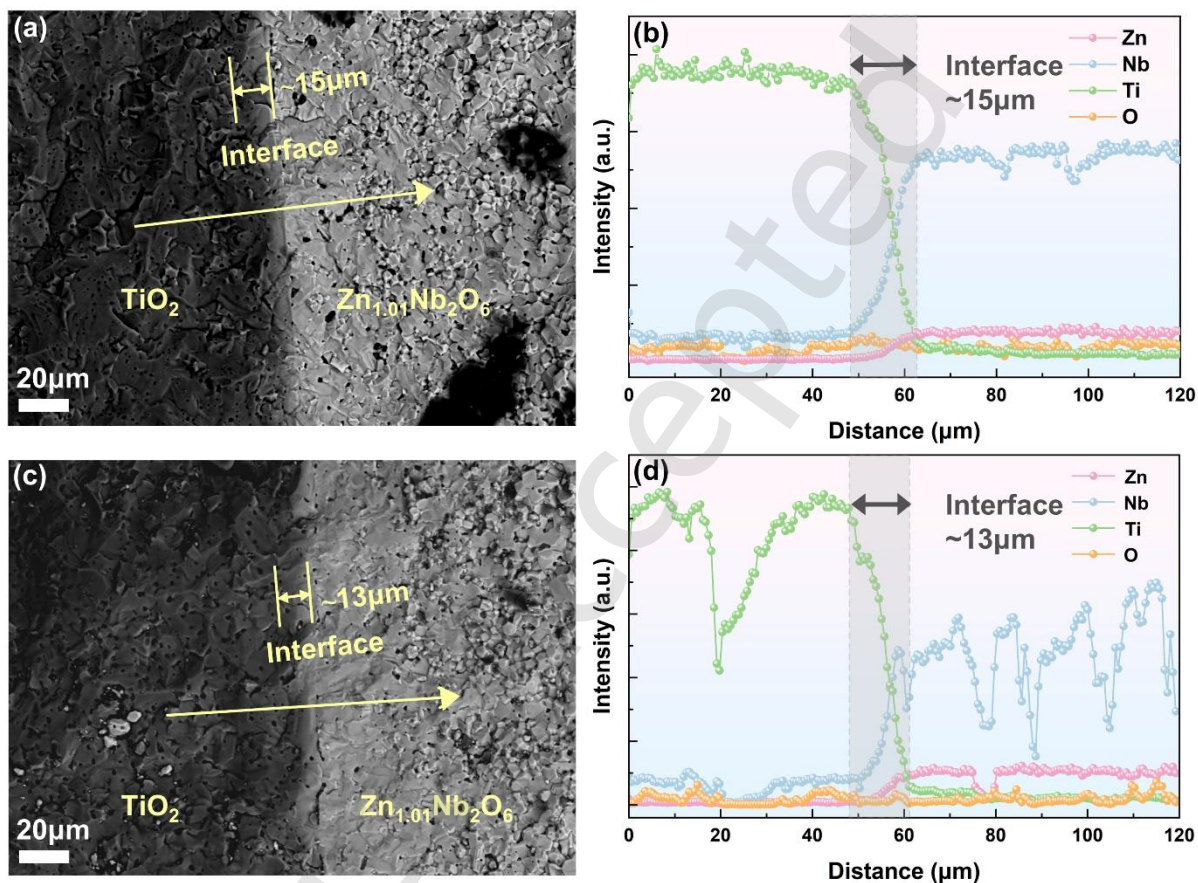


Fig. 2 Fracture-surface BSE images and the corresponding EDS line-scan profiles of the ZNO-TO core-shell cofired ceramics with (a, b) green TO cores and (c, d) fired TO cores.

EDS line scans across the ZNO/TO interfaces are shown in Figs. 2(b) and 2(d). Within the spatial resolution of EDS, Ti decreases monotonically from the TO core toward the ZNO shell, while Zn and Nb increase. The graded-region width is approximately 15 μm for green TO cores and 13 μm for fired TO cores, respectively. Apart from this small difference, the two architectures show similar interdiffusion profiles, indicating that the initial sintering state of the TO cores has a very limited influence on the final ZNO-TO interfaces.

The core-shell geometry confines the temperature-compensating phase to a compact central region while preserving a continuous ZNO shell. This spatial design allows a small amount of core material to adjust τ_f , whereas most of the resonator remains the low-loss ZNO phase and retains a high $Q \times f$ value. The limited interdiffusion observed by EDS is spatially restricted and does not alter the primary structural function of the architecture. Without obvious cracks, interfacial separations, and additional secondary phases, good cofiring compatibility can be obtained under the present conditions.

3.1.3 Microwave dielectric properties

Figure 3 presents the microwave dielectric properties (ϵ_r , $Q \times f$, and τ_f) of the ZNO-TO core-shell cofired ceramics as a function of TiO_2 core content. The data for the samples with unsintered TiO_2 cores (labeled as “Green TO”) and pre-sintered TiO_2 cores (labeled as “Fired TO”) were plotted together for comparison.

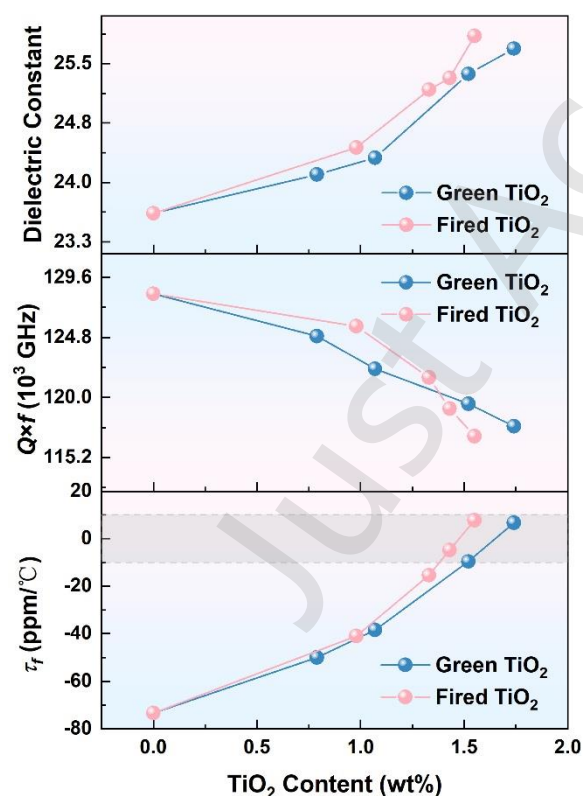


Fig. 3 Microwave dielectric properties (ϵ_r , $Q \times f$, and τ_f) of the ZNO-TO core-shell cofired ceramics as a function of green or fired TiO_2 core content.

The two series exhibit highly similar trends: ϵ_r and τ_f increase systematically with rising TiO_2 core content, while the $Q \times f$ value decreases correspondingly. Notably, even a small core fraction of TiO_2

effectively tunes τ_f to near zero with only a marginal degradation in $Q \times f$ values. The ZNO-TO ceramics show favorable microwave dielectric performance. For green TO cores, the 1.52 wt% sample exhibits $\epsilon_r \sim 25.37$, $Q \times f \sim 119,500$ GHz, and $\tau_f \sim -9.6$ ppm/°C, while the 1.74 wt% sample exhibits $\epsilon_r \sim 25.69$, $Q \times f \sim 117,700$ GHz, and $\tau_f \sim +6.7$ ppm/°C. Similar compensation is obtained with fired TO cores: the 1.43 wt% sample exhibits $\epsilon_r \sim 25.32$, $Q \times f \sim 119,100$ GHz, and $\tau_f \sim -4.8$ ppm/°C; and the 1.55 wt% sample exhibits $\epsilon_r \sim 25.85$, $Q \times f \sim 116,900$ GHz, and $\tau_f \sim +7.7$ ppm/°C. The two ZNO-TO series exhibit similar microwave dielectric trends, indicating that the initial sintering state of the TO core has only a limited effect on the overall microwave dielectric response. This behavior is consistent with the similar interdiffusion widths in Fig. 2. Localizing the heterogeneous interface helps preserve the continuous ZNO framework and its high $Q \times f$ value while the TO core adjusts τ_f .

Meanwhile, the core-shell cofired samples have relative densities above 97% (Fig. S8), confirming good sintering densification and a low overall pore fraction. Although pores can lower ϵ_r and $Q \times f$ in principle, the high and narrowly distributed relative densities indicate that porosity is not a significant factor in the observed dielectric-property trends. Therefore, the changes in ϵ_r , $Q \times f$, and τ_f are attributed primarily to the designed core-shell architecture and the amount of temperature-compensating core material. Basically, the heterogeneous resonator can be described by the electric-energy filling factor of each phase. Thus, a phase contributes to the overall microwave dielectric performance according to its permittivity, volume, connectivity, and overlap with the local electric field, rather than according to mass fraction alone [23,43-46]. Because rutile TO has a much higher ϵ_r and a much larger positive τ_f than ZNO [29,30,33-35], even a small TO core can provide finite electric-energy participation. Increasing the core content increases this participation and therefore raises ϵ_r and shifts τ_f toward positive values, consistent with Fig. 3.

3.1.4 Simulation

To gain deeper insights into the excellent microwave dielectric performance of the core-shell ceramic architectures, the electric field distribution and quality factor were analyzed using the HFSS

eigenmode solver. Figure 4 presents the corresponding simulation results for different architectures.

Figure 4(a) shows the cavity, supports, and core-shell resonator. Figure 4(b) compares measured and simulated $Q \times f$ values for fired-TO cores. The similar trends support the use of the model to interpret field participation; the remaining difference is expected as conductor, support, radiation, porosity, grain-boundary, and other extrinsic losses were not included in the idealized eigenmode calculation.

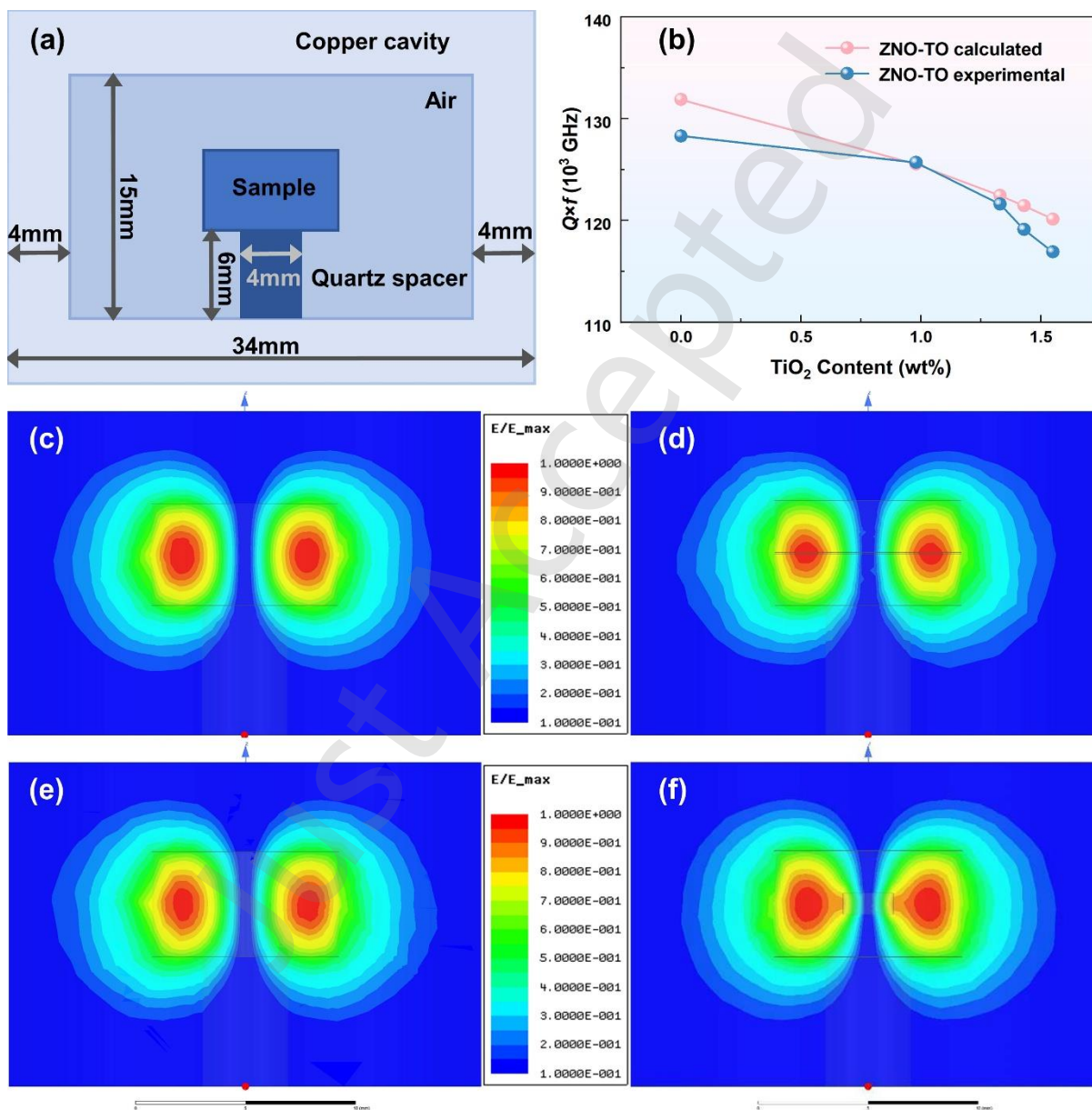


Fig. 4 HFSS eigenmode simulation results: (a) schematic of the simulation model, (b) measured and simulated $Q \times f$ values for the ZNO-TO core-shell ceramics; electric field distribution: (c) $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$, (d) ZNO/TO/ZNO, (e) ZNO-TO coaxial cylinder, and (f) ZNO-TO core-shell architecture.

The simulated electric field (E -field) distributions for different ceramic architectures are presented in Figs. 4(c)-4(f). For reference, Figure 4(c) shows the E -field distribution for the unmodified $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ ceramic cylinder. Notably, the E -field intensity is minimized along the z -axis of the cylinder, a region that constitutes the “dead zone” of the electric field. Figure 4(d) displays the E -field distribution for the ZNO/TO/ZNO trilayer architecture. The E -field pattern resembles a compressed version of the reference in Fig. 4(c), with the field lines concentrating predominantly around the central TiO_2 layer. To situate the TiO_2 layer entirely within the dead zone of the matrix ZNO, a coaxial cylinder structure (a TiO_2 cylinder concentrically surrounded by a $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ annulus) was simulated. As shown in Fig. 4(e), this architecture yields an E -field distribution virtually identical to that of the pure matrix, representing the theoretical optimum for minimizing perturbation in the E -field distribution. However, the practical fabrication of such a precise coaxial ceramic structure is exceptionally challenging.

Based on the field distributions and fabrication feasibility, the compact rectangular TO core was placed at the geometric center of the cylinder near the axial low-field region. As shown in Fig. 4(f), this placement changes the local field around the core while leaving the predominant annular field in the continuous ZNO shell similar to that of pure ZNO. Thus, core morphology and position regulate the overlap between the compensator and the resonant field rather than changing the $\text{TE}_{01\delta}$ mode topology. This core-shell cofiring design effectively mitigates the detrimental impact on the $Q \times f$ value, offering an effective approach to synergistically optimize the microwave dielectric properties.

3.2 General applicability and advantages of artificial core-shell cofiring strategy

3.2.1 Application to ZNO-CTO and ZNO-STO core-shell cofired ceramics

To examine transferability across compensators, ZNO-CTO and ZNO-STO core-shell ceramics were prepared subsequently. The XRD patterns of the core samples are shown in Fig. S9. Both the CaTiO_3 ceramics sintered at 1300 °C for 4 h and the CaTiO_3 powders calcined at 1150 °C for 4 h exhibit the pure perovskite phase (PDF#00-042-0423) without any secondary phases. Similarly, the patterns of

the sintered SrTiO₃ ceramics and calcined SrTiO₃ powders match the single-phase cubic perovskite structure (PDF#00-035-0734). The ZNO-CTO cross-sectional BSE image and EDS line scan are selected to show in Fig. S10. The ZNO-CTO interface contains an approximately 100 μm graded region, which is wider than that of ZNO-TO.

Figure 5 summarizes the microwave dielectric properties of ZNO-CTO and ZNO-STO ceramics containing green or pre-sintered cores. In ZNO-CTO, ϵ_r and τ_f increase with CTO content, whereas $Q \times f$ decreases. The 0.74 wt% green-CTO sample exhibits $\epsilon_r \sim 24.89$, $Q \times f \sim 79,400$ GHz, and $\tau_f \sim -2.9$ ppm/ $^{\circ}\text{C}$; the 1.04 wt% fired-CTO sample exhibits $\epsilon_r \sim 25.09$, $Q \times f \sim 67,800$ GHz, and $\tau_f \sim -4.5$ ppm/ $^{\circ}\text{C}$. In ZNO-STO, increasing the green-STO core content similarly raises ϵ_r and τ_f while lowering $Q \times f$. The sample with a 0.55 wt% green STO core exhibits $\epsilon_r \sim 24.81$, $Q \times f \sim 72,500$ GHz, and $\tau_f \sim +8.2$ ppm/ $^{\circ}\text{C}$, confirming that a small STO core can also provide effective temperature compensation.

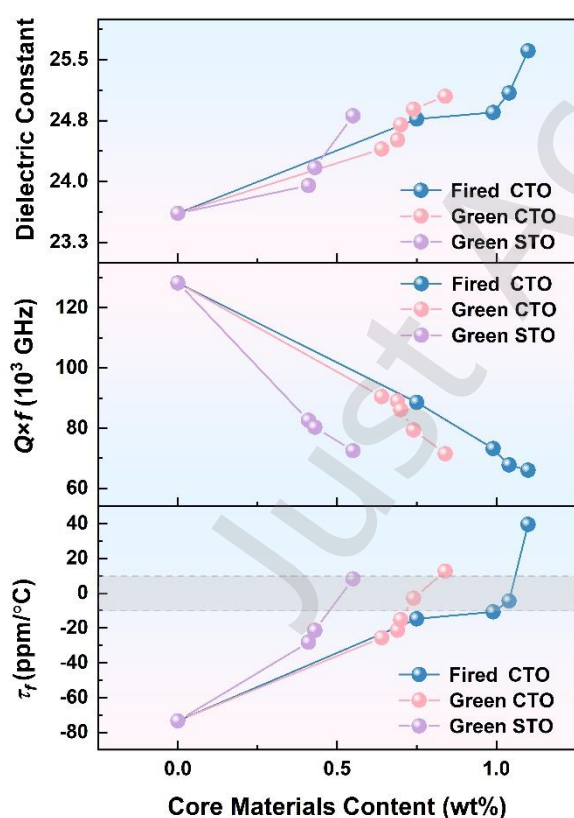


Fig. 5 Microwave dielectric properties (ϵ_r , $Q \times f$, and τ_f) of ZNO-CTO and ZNO-STO core-shell ceramics.

3.2.2 Advantages in regulating microwave dielectric performance

As for the modification of ZNO through conventional ion substitution, the regulation of microwave dielectric properties remains coupled to many factors including defect chemistry, lattice distortion, and sintering behavior. This coupling makes it difficult to adjust temperature stability independently while preserving the intrinsic high $Q \times f$ value of ZNO. As for the conventionally mixed $(1-x)\text{ZnNb}_2\text{O}_6-x\text{TiO}_2$ ceramics, the system requires approximately 58-60 mol% TO to obtain near-zero τ_f , with reported $Q \times f$ values of approximately 6,000-48,000 GHz [33,46-48]. The layer-cofiring process separates ZNO and TO into discrete regions and confines their chemical interaction to narrow planar interfaces, and good microwave dielectric characteristics could be achieved in the ZNO/TO/ZNO architectures [11]. As the content of temperature compensators for regulating near-zero τ_f is relatively low, the thin thickness of middle planar layer could increase the risk of cofiring mismatch of sandwich-structure ceramics as different sintering behaviors of the end-layer members.

As for the proposed core-shell architectures, the cofiring behavior can be further optimized by replacing the full-area TiO layer with a compact internal core that is completely surrounded by a three-dimensional continuous ZNO shell. In this case, the mass transportation (including underlying chemical reaction) and sintering mismatch between heterogeneous layers can be well confined inside the ceramics along core-shell interfaces, which is beneficial to obtaining good appearance configuration. The physical regulation mechanism of the present core-shell architecture mainly originates from the spatially selective participation of the constituent ceramics in the resonant electromagnetic mode, rather than factors of conventional material concept including phase composition, particle size, grain size, grain boundary, porosity, defect [47,49,50]. Unlike the planar TO layer that intersects the high-field annular region, the compact core is positioned near the central axis, where the electric-field intensity of the resonant mode is relatively weak. This positioning provides a structural basis for suppressing the loss contribution of TO and retaining the high $Q \times f$ value of the ZNO matrix to some extent while the overall τ_f is adjusted.

The microwave dielectric properties ($Q \times f$ values and τ_f) of ZnNb_2O_6 -based ceramics are summarized in Fig. 6 and Table S2 [11,46-48, 51-66]. The $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ -based core-shell ceramics exhibit competitive microwave dielectric performance among reported ZnNb_2O_6 -based systems. Their moderate permittivity, low loss, and temperature stability make them promising for resonators, filters, and oscillators in advanced 5G/6G and satellite-communication systems.

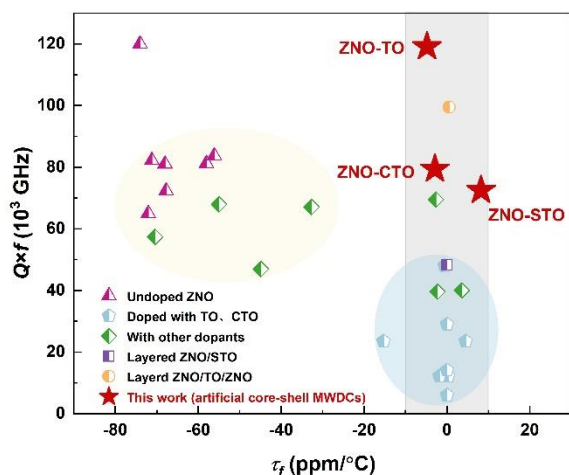


Fig. 6 Microwave dielectric properties ($Q \times f$ values and τ_f) of the ZnNb_2O_6 -based ceramics. Data were collected from the literature [11,46-48, 51-66].

3.3 Device design and simulation

Dielectric resonator antennas are promising for advanced wireless systems because of their low loss, high radiation efficiency, and design flexibility. The measured dielectric parameters of the optimized ZNO-TO ceramic with a 1.43 wt% pre-sintered TO core were used as input values for the design and simulation of a cylindrical dielectric resonator antenna (CDRA).

The antenna geometry is shown in Figs. 7(a) and 7(b), and the simulated co- and cross-polarized radiation patterns at 4.31 GHz are shown in Figs. 7(c) and 7(d). The HFSS model predicts a 40 MHz impedance bandwidth (4.287-4.327 GHz), a minimum return loss of -43 dB, and a VSWR of ~ 1.015 at the center frequency. It also predicts radiation efficiency above 90% across the operating band and a peak realized gain of 6.13 dBi at 4.31 GHz. The observations can serve as a preliminary numerical

feasibility assessment of the CDRA prototype based on the core-shell cofired ceramics for potential C-band applications.

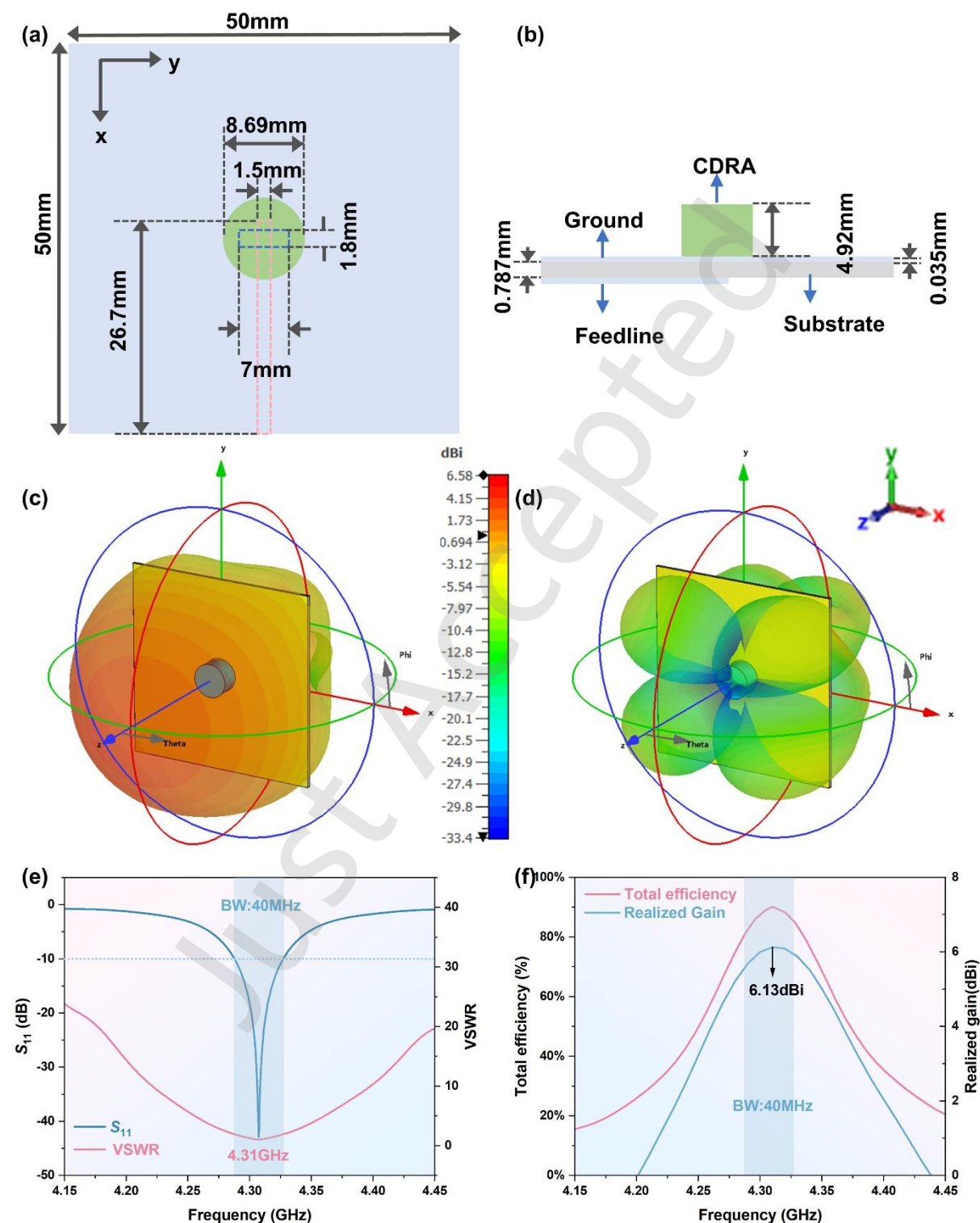


Fig. 7 Geometry and dimensions of the simulated CDRA: (a) top view and (b) side view; simulated three-dimensional radiation patterns: (c) co-polarized and (d) cross-polarized at 4.31 GHz; (e) simulated S_{11} and VSWR; and (f) simulated total efficiency and realized gain.

4 Conclusions

This study developed an artificial core-shell cofired architecture using a continuous $\text{Zn}_{1.01}\text{Nb}_2\text{O}_6$ shell and localized TO, CTO, or STO temperature-compensating cores. Overall XRD of representative ZNO-TO core-shell ceramics detected only columbite ZNO and rutile TO, whereas EDS revealed a narrow 13-15 μm compositionally graded interface, which could be interpreted as limited interdiffusion and possible local solid-solution formation. Positioning the compact core near the axial low-field region of the $\text{TE}_{01\delta}$ mode limited its loss contribution while allowing temperature compensation. The optimized 1.43 wt% fired-TO sample achieved $\epsilon_r \sim 25.32$, $Q \times f \sim 119,100$ GHz, and $\tau_f \sim -4.8$ ppm/ $^\circ\text{C}$. Importantly, this core-shell cofired strategy was generally applicable for ZNO-CTO and ZNO-STO core-shell systems, which achieved $Q \times f \geq 67,800$ GHz while maintaining near-zero τ_f . The CDRA simulation validated the additional application potential of the ZNO-TO core-shell ceramic, with excellent impedance matching (VSWR ~ 1.015), high radiation efficiency ($>90\%$), and a peak realized gain of 6.13 dBi. Therefore, this artificial core-shell architecture strategy unlocks the potential of conventional MWDCs, paving the way for temperature-stable and low-loss components in advanced 5G/6G and satellite communication systems.

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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

Supplementary figures (Figs. S1-S10) and tables (Tables S1-S2) are available in the online version of this article.

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