



# Boosting densification and microwave dielectric properties in cold sintered BaF<sub>2</sub> ceramics for 5.8 GHz WLAN applications

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## ABSTRACT

BaF<sub>2</sub> is a low-firing fluoride with excellent microwave dielectric properties, while the densification of BaF<sub>2</sub> ceramics is challenging via conventional sintering. In this work, dense BaF<sub>2</sub> ceramics with 95.3–98.5% relative densities have been prepared via the cold sintering (150–600 MPa, 150 °C, 1 h) and following post-annealing at 900 °C. The scanning electron microscope images demonstrate closely packed microstructures, and the chemical compatibility between BaF<sub>2</sub> ceramics and Ag electrodes is identified. The optimum *Qf* (82,320 GHz) is 1.53 times higher than that obtained via conventional sintering (53,654 GHz), with a dielectric permittivity,  $\epsilon_r = 7.3$ , and a temperature coefficient of resonant frequency,  $\tau_f = -107.9$  ppm/°C. Furthermore, a BaF<sub>2</sub>-based microstrip patch antenna is fabricated, which realizes an  $S_{11} = -16.5$  dB, a high gain of 5.84 dB, and total efficiency of  $-0.38$  dB at 5.78 GHz. The exceptional microwave dielectric properties and antenna performances indicate that BaF<sub>2</sub> ceramics are promising candidates for 5.8 GHz wireless local area network applications.

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## 1. Introduction

The ongoing wave of network transformation is fueled by the rapid development of wireless communication technology. The rapidly deployable technology has given modern society the ability to extend networking communications in areas where traditional wiring may be too expensive or impossible. The wireless local area network (WLAN) is one of the most popular routes in constructing wireless networks. The carrier frequencies of WLAN include the lower-frequency band of 2.4 GHz (2.4–2.484 GHz) and the higher-frequency band of 5.8 GHz (5.725–5.825 GHz) [1,2]. Nowadays, the 2.4 GHz band is becoming crowded owing to the dramatic growth of wireless communication demands. Many users opt to use the 5.8 GHz band since it provides more spectrums and encounters less interference.

Microwave dielectric ceramics have established their status in wireless communication systems by improving the size and

packaging density of microwave integrated circuits [3–5]. For antenna substrate applications, the crucial characteristics of microwave dielectric ceramics are low dielectric permittivity ( $\epsilon_r$ ), high quality factor (*Qf*), and near-zero temperature coefficient of the resonant frequency ( $\tau_f$ ). Besides, a low densification temperature (<960 °C) allows ceramics to cofire with conductive electrodes (such as Ag), offering the ability to be applied in the low temperature cofired ceramic (LTCC) technology [5–7].

According to the Clausius-Mossotti equation,  $\epsilon_r$  is determined by the ionic polarizability per volume [8]. Hence, the search of the low- $\epsilon_r$  materials is mainly focused on oxides with low polarizabilities (such as silicates, aluminates, and borates [9–14]). Recently, researchers have expanded the low- $\epsilon_r$  materials to fluorides since F has a lower ionic polarizability of 1.62 Å<sup>3</sup> than that of O (2.01 Å<sup>3</sup>) [15]. Geyer et al. prepared a series of fluoride single crystals and reported excellent dielectric performances at the microwave frequency range [16]. Zhang et al. reported a novel low-loss Li<sub>5</sub>Ti<sub>2</sub>O<sub>6</sub>F ceramics and identified their potential applications in LTCC technology [17]. Song et al. prepared the low-fired BaF<sub>2</sub> ceramics through conventional sintering (CS) at 925 °C and reported a low  $\epsilon_r$  of 6.72 and an acceptable *Qf* value of 53,654 GHz [18]. Meanwhile, owing to the gas entrapment and the low driving force of densification during CS, the

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optimal relative density of the conventional sintered BaF<sub>2</sub> ceramics was only 92.04%. [18]. Given that the porous microstructure is notoriously harmful to the *Qf* values, the optimization of densification in BaF<sub>2</sub> ceramics may trigger a breakthrough in the development of low-loss fluorides.

Cold sintering is a novel low-temperature consolidation technique that applies high pressures (hundreds of MPa) to accelerate the grain boundary/surface diffusion and mass transport [19,20]. Recent work on ultra-low temperature (below 200 °C) densification via cold sintering is mainly focused on components with high solubilities (usually in water), such as Li<sub>2</sub>MoO<sub>4</sub> (44.8 g/100 mL), NaCl (36 g/100 mL), and H<sub>3</sub>BO<sub>3</sub> (5.80 g/100 mL) [14,21,22]. For the insoluble compounds such as BaTiO<sub>3</sub>, K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>, and TiO<sub>2</sub>, a following post-annealing treatment is generally required [23–25]. Hence, given the great potential of performance improvement and the low solubility (0.161 g/100 mL) of BaF<sub>2</sub> [26], BaF<sub>2</sub> ceramics are prepared via a cold sintering process followed by a subsequent post-annealing at 900 °C. The densification, microwave dielectric properties, and their chemical compatibility with Ag electrodes are systematically investigated. Moreover, a BaF<sub>2</sub>-based microstrip antenna operating at 5.8 GHz is designed and fabricated to identify their potential WLAN applications. The return loss, radiation pattern, gain, and total efficiency of the BaF<sub>2</sub>-based antenna are measured and compared with the simulated ones.

## 2. Experimental procedure

Prior to weighing, BaF<sub>2</sub> raw powder with high purity (99.99%) was placed into the oven and dried overnight at 150 °C. After drying, the powder was homogeneously mixed with 10 wt% of deionized water and then cold sintered under the pressures of 150–600 MPa. The uniaxial pressure for the BaF<sub>2</sub> substrate was 600 MPa. The cold sintering temperature and dwelling time were fixed as 150 °C/1 h. The dimensions of the as-cold sintered pellets were 12.7 mm in diameter and ~5 mm in height. The as-cold sintered pellets were then post annealed at 900 °C for 3 h to achieve further densifications.

The relative density was evaluated using the Archimedes method. The room-temperature X-ray diffraction (XRD) patterns were recorded using a RIGAKU D/MAX 2550/PC diffractometer. The XRD data for Rietveld refinement was collected with a scanning step size of 0.02° and a counting time of 1 s. The microstructures of the polished and thermally etched (875 °C/1 h) surfaces of BaF<sub>2</sub> ceramics were observed using a Zeiss Sigma 300 scanning electron microscopy (SEM). The microwave dielectric properties and the *S*<sub>11</sub> curve of the fabricated antenna were evaluated using a Keysight N5234B network analyzer. The measured resonant frequency of the BaF<sub>2</sub> ceramics was around 11 GHz.  $\epsilon_r$  and  $\tau_f$  values were measured using the parallel-plate method [11]. *Qf* value was evaluated using the resonant cavity method [12]. The design and simulation of the proposed antenna were conducted using the Computer Simulation Technology (CST) software. The radiation patterns were measured in a STIMO SG24 microwave anechoic chamber.

## 3. Results and discussion

The XRD patterns of BaF<sub>2</sub> raw powder and ceramics obtained under various uniaxial pressures are shown in Fig. 1(a). All the diffraction patterns can be well indexed based on the standard PDF card of BaF<sub>2</sub> (JCPDS #85–1342), indicating that no phase transformation occurs during the cold sintering and post-annealing processes. Moreover, the shape and position of each diffraction peak remain stable with the increasing uniaxial pressures, suggesting that the uniaxial pressure has little effect on the structural parameters. Rietveld refinement of the XRD data is conducted to further identify the crystal structure, and the results are shown in Fig. 2(b). The

crystal structure of cubic BaF<sub>2</sub> with a space group of Fm-3m. is adopted as the structural model. The calculated pattern is in good agreement with the measured one, which can be confirmed from both the low amplitude of the different line and the satisfactory results of the reliability factors ( $R_p = 7.98\%$ ,  $R_{wp} = 11.3\%$ , and  $\chi^2 = 6.43$ ).

The SEM images of BaF<sub>2</sub> ceramics obtained under various uniaxial pressures are shown in Fig. 2(a)–(d), respectively. Dense and uniform microstructures with distinct grain boundaries can be found in the present ceramics. Some tiny pores at the grain boundary junctions are observed in Fig. 2(a) and (b) and disappear under higher uniaxial pressures. The grain size distributions and average grain sizes are insensitive to the uniaxial pressure, which are identified from the distribution curves shown in Fig. 2(e–h). Furthermore, the cold-sintered BaF<sub>2</sub> ceramics and Ag colloids are cofired at 900 °C to identify the chemical compatibility between BaF<sub>2</sub> and metallic electrodes. Fig. 2(i) and (j) show the XRD pattern and SEM image of the BaF<sub>2</sub>-Ag ceramics, respectively. The XRD pattern exhibits an independent existence of BaF<sub>2</sub> and Ag composites, and no other secondary phases are observed. Besides, the SEM image demonstrates a distinct boundary between the two phases, which is further confirmed by the concentration profiles on both sides of the interface. Hence, it is reasonable to conclude that BaF<sub>2</sub> ceramics exhibit excellent chemical compatibility with Ag electrodes, which is promising for applications in the LTCC technology.

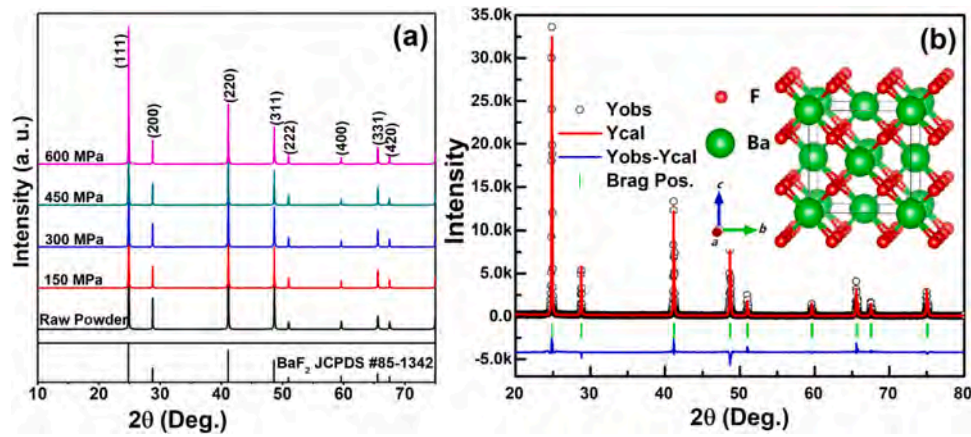
Fig. 3 shows the variation of the relative density and microwave dielectric properties of BaF<sub>2</sub> ceramics. With increasing the uniaxial pressure, the relative density ascends progressively from 95.3% at 150 MPa to 98.5% at 600 MPa, indicating the crucial role of uniaxial pressure in improving the densification.  $\epsilon_r$  increases from 7.05 at 150 MPa to 7.30 at 600 MPa, and all the values are higher than that obtained via CS (6.72). On the other hand, the variation of  $\epsilon_r$  follows the same trend as the relative density, indicating that  $\epsilon_r$  should be mainly dominated by the porosity (*P*). According to Penn et al., the porosity corrected permittivity ( $\epsilon_{cor}$ ) can be calculated using Eq. (1) to exclude the effects of porosity [27].

$$\epsilon_r = \epsilon_{cor} \left( 1 - \frac{3P(\epsilon_{cor} - 1)}{2\epsilon_{cor} + 1} \right) \quad (1)$$

As shown in Table 1, the calculated  $\epsilon_{cor}$  values remain stable at approximately 7.45, further demonstrating the decisive role of porosity in controlling  $\epsilon_r$ .

The *Qf* value increases from 72,350 GHz at 150 MPa to 80,400 GHz at 300 MPa and remains relatively stable at higher pressures. The optimal *Qf* value (82,320 GHz) is 53.4% higher than that via CS (53,654 GHz) [18]. Since the present ceramics share the same chemical composition, the variation of the *Qf* value in this work should be dominated by the extrinsic parameters such as pores, grain boundaries, and secondary phases [28,29]. With the absence of impurities and apparent grain size change, the improvement of the *Qf* should be mainly ascribed to the enhancement of densification. The  $\tau_f$  value varies relatively stable with the increasing uniaxial pressure, and all the values remain at approximately −106 ppm/°C. The optimal microwave dielectric properties ( $\epsilon_r = 7.3$ , *Qf* = 82,320 GHz and  $\tau_f = -109.4$  ppm/°C) are obtained under the applied pressure of 600 MPa.

The major component of the WLAN system is the antenna. The microstrip patch antennas gain widespread popularity among antennas due to their merits of low cost, low profile, and easy fabrication [30,31]. Fig. 4(a) shows the schematic figure of the designed patch antenna. A rectangular BaF<sub>2</sub> ceramic with dimensions of 20 × 20 × 1 mm is adopted as the substrate. The patch, microstrip transmission line, and ground plane are made of commercial copper foil with a thickness of 0.06 mm. The dimensions of the patch (width (*w*) and length (*l*)) are calculated based on the following equations



**Fig. 1.** (a) The XRD patterns of BaF<sub>2</sub> raw powder and ceramics in this work. (b) The measured (circles) and calculated (red lines) XRD patterns of BaF<sub>2</sub> ceramics obtained under the uniaxial pressure of 450 MPa. The inset shows the calculated crystal structure of BaF<sub>2</sub> ceramics.

and then trimmed based on the simulation results to achieve resonance at the desired 5.8 GHz [5].

$$w = \frac{c}{2f_0} \sqrt{\frac{2}{\epsilon_r + 1}} \quad (2)$$

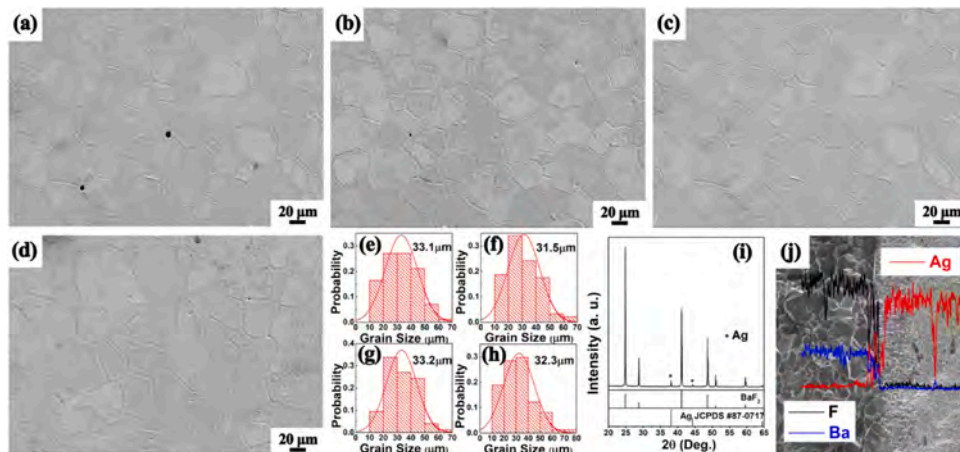
$$l = \frac{c_0}{2f_0 \sqrt{\epsilon_{eff}}} \quad (3)$$

$$\epsilon_{eff} = \frac{\epsilon_r + 1}{2} + \frac{\epsilon_r - 1}{2} \left( \frac{1}{\sqrt{1 + 12H/w}} \right) \quad (4)$$

where,  $c$  is the velocity of light in vacuum,  $f_0$  is the designed resonant frequency,  $\epsilon_{eff}$  is the effective permittivity, and  $H$  is the substrate's height. The geometric dimensions and the front/rear views of the BaF<sub>2</sub>-based antenna are shown in Fig. 4(a–c). The  $S$  parameters describe the input-output power relations and are the most commonly quoted parameters in evaluating the antenna performances. The measured and simulated  $S_{11}$  curves are plotted in Fig. 4(d). The  $S_{11}$  value defines the percentage of the power reflected from the antenna and is also known as the return loss. The measured  $S_{11}$  curve matches well with the simulated one, with the optimum value of  $-16.5$  dB at the resonant frequency of 5.78 GHz. The measured resonant frequency is slightly lower than the simulated 5.80 GHz, which can be attributed to the fringing fields around the antenna

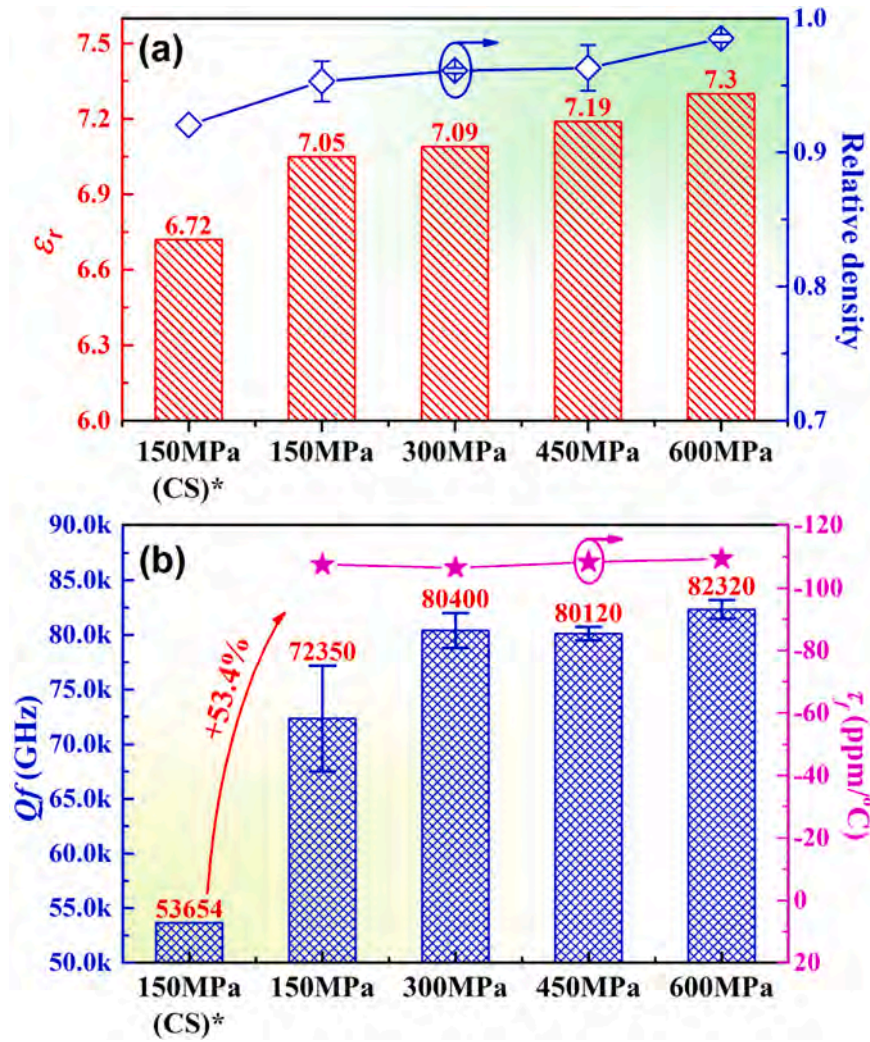
[32].  $S_{11} = -10$  dB denotes that 90% of the power is radiated through the antenna. Hence,  $-10$  dB is widely accepted as the base value for antenna applications. In this work, the BaF<sub>2</sub> based antenna presents a simulated  $-10$  dB bandwidth of 152 MHz and a measured bandwidth of 96 MHz. According to Xiang et al., the difference in bandwidth can be ascribed to the ambient humidity and the SMA connector's soldering [5]. The Voltage Standing Wave Ratio (VSWR) is another crucial factor that numerically describes the impedance matching. The VSWR is always real and positive, and a value in the range of 1.0–1.5 is considered satisfactory for antenna applications. Fig. 4(e) plots the VSWR curve as a function of the frequency, where an excellent value of 1.35 is obtained at 5.78 GHz. Therefore, the fabricated antenna conforms to the expected properties and is compatible with the 5.8 GHz WLAN applications.

Fig. 5(a) shows the simulated upward and downward 3D far-field radiation patterns of the BaF<sub>2</sub>-based antenna at 5.8 GHz. The fabricated antenna is a directional antenna with one main lobe radiating out from the patch side, and the maximum gain is 4.99 dB. The radiation patterns of the two principal planes (E- and H- planes) can be obtained by making two slices through the 3D pattern ( $xoz$  and  $yoz$  planes). Fig. 5(b, c) show the antenna measurement setup in the microwave anechoic chamber, where the radiation patterns are measured to compare with the simulated ones (see Fig. (d) and (e)). The measured and simulated patterns in both planes are in good agreement, where the maximum gain of 5.84 dB is measured at the



**Fig. 2.** Microstructures of BaF<sub>2</sub> ceramics prepared under various uniaxial pressures (a) 150 MPa, (b) 300 MPa, (c) 450 MPa, and (d) 600 MPa. (e–h) The corresponding grain size distributions and average grain sizes of Fig. (a)–(d). (i) XRD pattern and (j) SEM image and EDS (energy dispersive spectra) line scan result of BaF<sub>2</sub>-Ag composite ceramics cofired at 900 °C.





**Fig. 3.** (a) The relative density and  $\epsilon_r$  of BaF<sub>2</sub> ceramics obtained under various uniaxial pressures. (b) The  $Qf$  and  $\tau_f$  values of BaF<sub>2</sub> ceramics as functions of the applied uniaxial pressure. \*The uniaxial pressure and microwave dielectric properties of the conventional sintered (CS) BaF<sub>2</sub> ceramics are cited from Ref. [18].

**Table 1**

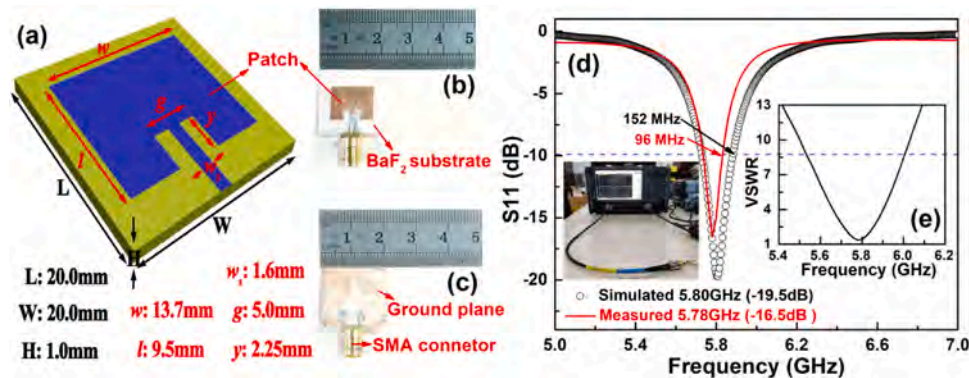
The relative densities and microwave dielectric properties of BaF<sub>2</sub> ceramics in this work.

Uniaxial pressure	$\rho$	$\epsilon_r$	$\epsilon_{cor}$	$Qf$ (GHz)	$\tau_f$ (ppm/°C)
CS-150 MPa	92.0%	6.72	7.44	53,654	-74.2
150 MPa	95.3%	7.05 ± 0.04	7.48	72,350 ± 4840	-107.5
300 MPa	96.1%	7.09 ± 0.03	7.44	80,400 ± 1600	-106.5
450 MPa	96.3%	7.19 ± 0.03	7.53	80,120 ± 610	-108.3
600 MPa	98.5%	7.3 ± 0.05	7.44	82,320 ± 870	-109.4

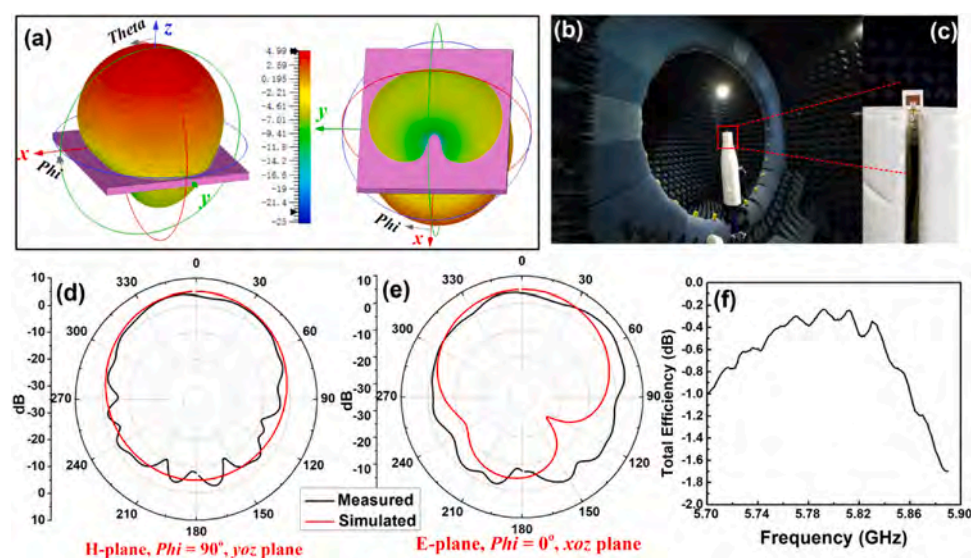
E-plane. The measured total efficiency of the BaF<sub>2</sub> antenna is plotted in Fig. 5(f), where the optimal value of -0.38 dB is obtained at 5.78 GHz. The total efficiency of an antenna is related to the power ratio using the following equation.

$$\text{dB} = 10 \times \lg(P_2/P_1) \quad (5)$$

where  $P_2$  is the power being measured, and  $P_1$  is the reference. According to Eq. (5), the fabricated BaF<sub>2</sub> antenna exhibits a power ratio



**Fig. 4.** (a) The dimensions and the (b) front and (c) rear views of the fabricated antenna. (d) The measured and simulated S<sub>11</sub> curves of the fabricated antenna. The S<sub>11</sub> curve is measured with the patch side upward (see the inset picture). (e) The VSWR curve in the frequency range of 5.4–6.2 GHz.



**Fig. 5.** (a) The simulated upward and downward 3D radiation patterns of the BaF<sub>2</sub>-based antenna at 5.8 GHz. (b,c) The setup of antenna measuring devices in the microwave anechoic chamber. The measured and simulated radiation patterns at the (d) H-plane and (e) E-plane. (f) The measured total efficiency of the fabricated antenna as a function of the frequency.

of 91.6% at 5.78 GHz. The total efficiency of the commercial WiFi antennas is typically in the range of  $-7$  to  $-1.5$  dB (power ratio 20–70%). The excellent performance in the present work should be ascribed to the high  $Q$  value of BaF<sub>2</sub> ceramics, as the total efficiency is sensitive to the dielectric loss of the substrates.

#### 4. Conclusions

BaF<sub>2</sub> ceramics with 95.3–98.5% relative densities have been prepared via the cold sintering (150–600 MPa, 150 °C, 1 h) and following post-annealings at 900 °C. The XRD and EDS results demonstrate satisfactory chemical compatibility between BaF<sub>2</sub> ceramics and Ag electrodes, suggesting the great application prospects in the LTCC technology. The optimal microwave dielectric properties ( $\epsilon_r = 7.3$ ,  $Q_f = 82,320$  GHz, and  $\tau_f = -109.4$  ppm/°C) are obtained under the applied uniaxial pressure of 600 MPa. The optimal  $Q$  value is 1.53 times greater than for conventionally sintered BaF<sub>2</sub> ceramics (53,654 GHz). A BaF<sub>2</sub>-based patch antenna is fabricated, which operates at 5.78 GHz with an  $S_{11}$  of  $-16.5$  dB. Good agreements between the measured and simulated results are obtained, and the designed antenna exhibits a satisfactory gain and total efficiency of 5.84 dB and  $-0.38$  dB, respectively. The excellent antenna performances conform to the expected properties, indicating that the cold sintered and post-annealed BaF<sub>2</sub> ceramics are promising candidates for 5.8 GHz WLAN applications.

#### CRediT authorship contribution statement

**Ding Hao Jin:** Investigation, Visualization. **Bing Liu:** Funding, Project administration, Supervision, Writing – review & editing. **Kai Xin Song:** Writing – review & editing. **Kui Wen Xu:** Software, Validation. **Yu Hui Huang:** Writing – review & editing. **Cheng Chao Hu:** Software, Validation. **Yuan Yun Hu:** Resources.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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