Crystal structure, microwave dielectric properties, and dielectric resonant antenna studies of novel low-permittivity CoAl₂O₄ spinel ceramics

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ABSTRACT

CoAl₂O₄ spinel ceramics were prepared via a standard solid-state reaction method, and their crystal structure, microwave dielectric properties, and dielectric resonant antenna applications were systematically investigated in this study. X-Ray diffraction patterns and Raman spectra confirmed that CoAl₂O₄ belongs to the Fd-3 m space group with cubic crystal symmetry. ε and Qf values increased with the increasing sintering temperature, where an ever-improving microstructure was also observed from the scanning electron micrographs. The optimal microwave dielectric properties were achieved as follows: εᵣ = 9.34, Qf = 30,500 GHz, and τf = −54 ppm/℃. Moreover, a dielectric resonant antenna was designed and simulated to demonstrate the application prospects of CoAl₂O₄ ceramics towards microwave antennas. The CoAl₂O₄-based antenna resonating at 14.33 GHz exhibited a high return loss of −40.9 dB, a wide impedance bandwidth of 940 MHz, and an exceptionally high total efficiency of 96.6%. The remarkable antenna performances suggested that CoAl₂O₄ ceramics were promising candidates for wireless communication devices operating at the Ku-band, provided τf can be further tuned toward zero.

1 Introduction

Wireless communication technology is fundamental to how we live, work, and play in the increasingly digital world. This trend has been building for decades and came to a head during the COVID-19 pandemic, when millions of us have come to depend on networks for packaged goods, entertainment, work—and still expect nearly immediate gratification. To meet those needs, the operating frequency of communication is expanding to the millimeter-wave region to offer a more efficient, secure, and flexible network [1, 2]. Microwave dielectric ceramics are critical components in wireless communication devices owing to the merits of low cost, excellent dielectric properties, and good thermal conductivity...
The dielectric permittivity ($\varepsilon_r$), quality factor ($Q_f$), and temperature coefficient of resonant frequency ($\tau_f$) are three fundamental parameters in evaluating microwave dielectric properties. For millimeter-wave applications, a low-permittivity ($\varepsilon_r < 10$) is preferred for high-speed signal transmission with minimum attenuation [5–7]. Moreover, high $Q_f$ and near-zero $\tau_f$ values are always desirable for satisfactory resonant frequency selectivity and temperature stableness, respectively.

Aluminates are promising low-$\varepsilon_r$ candidates owing to the relatively low ionic polarizability of Al$^{3+}$ (0.79 Å$^3$) [8]. Among these, spinels with the general formula of MAI$_2$O$_4$ (M = transition metals) have been extensively investigated owing to their easy preparation and low dielectric loss [9, 10]. Surendran et al. reported the microwave dielectric properties of ZnAl$_2$O$_4$ ceramics for the first time, where the optimal properties ($\varepsilon_r = 8.5$, $Q_f = 56,300$ GHz, $\tau_f = -79$ ppm/$^\circ$C) were obtained when sintered at 1425 $^\circ$C [9]. Meanwhile, similar microwave dielectric properties with $\varepsilon_r = 8.75$, $Q_f = 68,900$ GHz, and $\tau_f = -75$ ppm/$^\circ$C were also obtained in MgAl$_2$O$_4$ ceramics [10]. On the other hand, the spinel structure is flexible to substitutions. Numerous cations and cation combinations can be accommodated to obtain extremely diversified spinel end-members [11, 12]. However, current studies on the dielectric properties of spinels are mainly focused on the most common Mg- and Zn-based compounds. Systematic studies on different spinel end-members are lacking in the literature.

Owing to the similar ionic radius of Co$^{2+}$ (0.65 Å) and Mg$^{2+}$ (0.67 Å), the substitution of Co$^{2+}$ for Mg$^{2+}$ has been widely conducted and confirmed effective in improving the sinterability and microwave dielectric properties. By partially substituting Mg with Co, Huang et al. reported that the (Mg$_{1-x}$Co$_x$)-Ti$_2$O$_4$ ceramics possess much higher $Q_f$ values than the Mg-end member [13]. For Mg-based spinels, Tsai et al. reported a significant improvement of $Q_f$ value by forming (Mg$_{1-x}$Co$_x$)Al$_2$O$_4$ solid solutions as well [14]. Meanwhile, Tsai et al. reported similar low-$\varepsilon_r$ values of around 9 in CoAl$_2$O$_4$ spinel ceramics as well [14], while a systematical investigation on their sintering behavior, structure, microwave dielectric properties and antenna applications is still lacking in the literature.

In this study, CoAl$_2$O$_4$ ceramics are prepared via a standard solid-state reaction method. The sintering behavior, crystal structure, microstructure are systematically investigated together with their effects on the microwave dielectric properties. Moreover, a CoAl$_2$O$_4$-based dielectric resonator antenna prototype is designed and simulated to further explore their antenna applications.

2 Experimental procedure

CoAl$_2$O$_4$ ceramics were prepared via a standard solid-state reaction method using high-purity CoO (99.99%) and Al$_2$O$_3$ (99.99%) powder as raw materials. First, the stoichiometrically weighted powder was ball-milled in ethanol media for 12 h. After drying, the mixture was sieved and then calcined at 1200 $^\circ$C for 3 h. Next, the calcined powder was re-milled and then pressed into pellets with 12 mm in diameter and 5 mm in height. Finally, the green pellets were sintered at 1450–1550 $^\circ$C for 3 h to obtain the dense CoAl$_2$O$_4$ ceramics.

The relative density of CoAl$_2$O$_4$ ceramics was evaluated using the Archimedes method. Room-temperature X-ray diffraction (XRD) patterns were collected using a Shimadzu XRD-700X diffractometer. The XRD data for Rietveld analysis was collected using the step-scan mode, with a step degree of 0.02° and a counting time of 2 s. The ceramic samples were carefully polished to a roughness of about 0.5 μm for Raman measurement. Room-temperature Raman spectra were recorded using an HR-800 LabRaman device (Jobin Yvon, Longjumeau, France). Ar$^+$ ion laser with an output power of 20mW was used as the excitation source. The polished and thermal etched surfaces of CoAl$_2$O$_4$ ceramics were observed using an S-3400 (Hitachi, Tokyo, Japan) scanning electron microscopy (SEM). The thermal etching process was carried out at 50 $^\circ$C lower than the sintering temperature for 0.5 h. The dimensions of the sintered CoAl$_2$O$_4$ ceramics were around 9.5 mm in diameter and 5 mm in height. The measured resonant frequency of the CoAl$_2$O$_4$ ceramics was around 11 GHz. The $Q_f$ value was evaluated by the resonant-cavity method [15], using a silver-coated cavity connected to an E8363B network analyzer (Agilent, Palo Alto, CA). $\varepsilon_r$ and $\tau_f$ values were measured using the parallel-plate method [16]. The measurement of $\tau_f$ value was organized in the temperature range of 20–80 $^\circ$C. The design and simulation of the dielectric resonant antenna were conducted using the commercially...
available Computer Simulation Technology (CST) software.

3 Result and discussion

Figure 1 shows the relative density of CoAl$_2$O$_4$ ceramics as a function of sintering temperature. CoAl$_2$O$_4$ ceramics exhibit a relatively large sintering temperature range, as dense ceramics with relative densities above 94.5% are achieved in the whole sintering temperature range. An abrupt increase of relative density from 94.7% at 1475 °C to 97.3% at 1500 °C is noticed and remains relatively stable with further increasing sintering temperature. On the other hand, CoAl$_2$O$_4$ spinels are commonly investigated as ceramic pigments owing to their intense blue color and peculiar optical properties [17, 18]. As shown in the inset of Fig. 1, the color of CoAl$_2$O$_4$ ceramics turns from navy blue at 1450 °C to dark blue at 1500 °C and 1550 °C, which further confirms the improvement of relative density with increasing sintering temperature.

Figure 2a shows the XRD patterns of CoAl$_2$O$_4$ ceramics sintered at various temperatures. All the diffraction patterns match well with the standard diffraction feature of CoAl$_2$O$_4$ (JCPDS card No. 44–0160), and the relevant indices of crystallographic planes are labeled. Furthermore, no apparent change of peak position and intensity is observed with the increasing temperature. Hence, monophasic CoAl$_2$O$_4$ ceramics have been successfully prepared in this study, and the crystal structure remains stable in the whole temperature range. To further explore the crystal structure, the XRD data of CoAl$_2$O$_4$ ceramics sintered at 1550 °C is refined based on the spinel structure with a space group of $Fd-3 m$. Figure 2b shows the measured and calculated diffraction profiles of CoAl$_2$O$_4$ ceramics. The refined atomic coordinates, thermal displacement parameters, and occupations are listed in Table 1.

The measured and calculated XRD patterns keep a good consistency, as confirmed by the flatness of the difference line ($Y_{\text{obs}} - Y_{\text{cal}}$). Moreover, the outstanding reliability factors ($R_p = 0.839\%$, $R_{wp} = 1.13\%$, $R_{exp} = 0.73\%$, and $\chi^2 = 2.37$) indicate that the adopted spinel structure is valid and the refined results are reliable. Based on the refined structural parameters, Fig. 3 demonstrates the crystal structure of CoAl$_2$O$_4$. There are two kinds of Wyckoff positions for cations, i.e., 8a (1/8, 1/8, 1/8) and 16d (1/2, 1/2, 1/2). The cations connect with the neighboring oxygen anions and form two types of oxygen polyhedrons (i.e., tetrahedron at 8a site and octahedron at 16d site). On the other hand, the structural formula of CoAl$_2$O$_4$ can also be expressed as $^{IV}(\text{Co}_{1-x}\text{Al}_x)^{VI}[\text{Co}_{x}\text{Al}_{2-x}]\text{O}_4$, where $^{IV}$ and $^{VI}$ represent the 8a and 16d site, respectively; $x$ is called the inversion parameter [19, 20]. For normal spinels such as ZnAl$_2$O$_4$ and MgAl$_2$O$_4$, $x$ equals 0. A value of $x = 2/3$ corresponds to a completely random cation distribution between 8a and 16d sites. The other spinels with $x$ between 0 and 2/3 are denoted as largely normal spinels or between 2/3 and 1 (largely inverse spinels). According to the occupation results listed in Table 1, CoAl$_2$O$_4$ ceramics is a largely normal spinel with the calculated $x$ value of 0.098. Co$^{2+}$ has a strong preference for tetrahedral 8a site and Al$^{3+}$ for octahedral 16d site, though the cation radius of Al$^{3+}$ (0.535 Å) is smaller than that of Co$^{2+}$ (0.65 Å).

On the other hand, Raman spectroscopy is a powerful tool in revealing information on the crystal structure, electronic structure, and lattice vibrations [21–23]. Figure 4 plots the Raman spectra of CoAl$_2$O$_4$ ceramics sintered at 1450 °C and 1550 °C, respectively. Both samples display similar Raman patterns with five obvious Raman active peaks. No apparent change of peak position and intensity is noticed, corresponding to the similar XRD patterns obtained at various sintering temperatures. For spinels, the irreducible representations that describe the vibration...
modes of each Wyckoff position can be written as follows [11, 24]:

8a site: \( F_{1u}(\text{IR}) + F_{2g}(\text{R}) \)

16d site: \( A_{2u}(\text{S}) + E_u(S) + F_{2u}(\text{S}) + 2F_{1u}(\text{IR}) \)

32e site: \( A_{1g}(\text{R}) + A_{2u}(\text{S}) + E_u(S) + E_g(\text{R}) + 2F_{2g}(\text{R}) + F_{1}(\text{S}) + F_{2u}(\text{S}) + 2F_{1u}(\text{IR}) \)

where the (R) and (IR) denote Raman- and infrared-active vibrational modes, respectively. The rest modes marked with (S) are silent. Therefore, the Raman active modes of CoAl\(_2\)O\(_4\) ceramics are \( 3F_{2g} + A_{1g} + E_g \). Besides, the three \( 3F_{2g} \) modes are labeled as \( F_{2g}(1) \), \( F_{2g}(2) \), and \( F_{2g}(3) \) based on their wavenumbers.

The wavenumbers of the Raman active peaks are obtained via fitting the spectra using a Lorentz function, and the results are consistent with the previous works [25–27]. The \( F_{2g}(1) \) mode at 202 cm\(^{-1}\) is assigned to the Co/Al-O\(_4\) tetrahedron translation [25]. The position of \( E_g \) mode is reported to have a reasonable correlation with the cation radius at the 8a site [11]. Hence, the \( E_g \) mode at 409 cm\(^{-1}\) is assigned to the symmetric bending motion of the oxygen atoms within the tetrahedron [26]. The \( F_{2g}(2) \) mode at 517 cm\(^{-1}\) is attributed to the Co/Al-O asymmetric stretching vibration in the tetrahedral sites [11, 26]. The literature is inconsistent regarding the vibration assignment for the \( F_{2g}(3) \) mode at 629 cm\(^{-1}\), which has been reported as either the anti-symmetric
stretching mode of the tetrahedron unit or an asymmetric bending motion of the oxygen bonded to the tetrahedral cation [27, 28]. Previous studies on the wavenumber of $A_{1g}$ mode demonstrate that the octahedral cation has a more significant effect than the tetrahedral cation [29, 30]. This justifies that the $A_{1g}$ mode at 785 cm$^{-1}$ is related to the Co/Al-O stretching vibration in the octahedron.

Figure 5 shows the SEM images and corresponding grain size distributions of CoAl$_2$O$_4$ ceramics sintered at various temperatures. The microstructure is getting dense with the increasing sintering temperature. Besides, an apparent increase of grain size from 0.88 μm at 1450 °C to 5.10 μm at 1550 °C is also noticed. The improvement of microstructure is in good agreement with the variation of relative density and should be mainly attributed to the increased driving force of grain growth.

Figure 6 shows the microwave dielectric properties of CoAl$_2$O$_4$ ceramics as functions of sintering temperature. $\varepsilon_r$ increases monotonously with the increasing sintering temperature, from 8.959.34 °C at 1450 °C to 9.34 °C at 1550 °C. The variation of $\varepsilon_r$ is in good agreement with the relative density, indicating that $\varepsilon_r$ should be mainly determined by the porosity ($P$). According to Alford et al. [31], the effect of porosity can be excluded using the following Eq. (1), and the porosity corrected values ($\varepsilon_{cor}$) are plotted in Fig. 6a. All the $\varepsilon_{cor}$ values maintain at around 9.6, confirming that the porosity mainly dominates $\varepsilon_r$ of the present ceramics.

$$\varepsilon_r = \varepsilon_{cor} \left(1 - \frac{3P(\varepsilon_{cor} - 1)}{2\varepsilon_{cor} + 1}\right)$$  \hspace{1cm} (1)

$Q_f$ value indicates a monotonous increase with the increasing sintering temperature, from 23,550 GHz at 1450 °C to 30,500 GHz at 1550 °C. Since no phase transformation is obtained as confirmed from the XRD patterns, the increase of $Q_f$ value should be mainly attributed to the optimization of microstructures as shown in the SEM images. The optimal $Q_f$ value of CoAl$_2$O$_4$ ceramics is lower than the normal spinels such as ZnAl$_2$O$_4$ (56,300 GHz) and MgAl$_2$O$_4$ (68,900 GHz). According to Tsai et al., the lower $Q_f$ value in CoAl$_2$O$_4$ ceramics should be attributed to the more random distributions of the cations occupying tetrahedral and octahedral sites, which could render the anharmonic phonon decay process in the ceramic crystal and degrade the quality factors [14]. The variation of $\tau_f$ value is insensitive to the sintering temperature, and all the values maintain at around $-54$ ppm/°C. The negative $\tau_f$ value of the present ceramics poses difficulties for practical applications, which can be further optimized via forming...
composite ceramics with components having positive $\tau_f$ values, such as TiO$_2$ ($\tau_f = +460$ ppm/$^\circ$C), CaTiO$_3$ ($\tau_f = +850$ ppm/$^\circ$C) [32, 33]. The optimal microwave dielectric properties with $\varepsilon_r = 9.34$, $Qf = 30,500$ GHz, and $\tau_f = -54$ ppm/$^\circ$C are obtained when sintered at 1550 $^\circ$C.

A dielectric resonator antenna (DRA) consists of a block of ceramic (dielectric resonator) mounted on a metal surface (ground plane). DRA offers attractive features compared to microstrip patch antennas, including higher gain and efficiency, wider bandwidth, and easier excitation [34, 35].

A CoAl$_2$O$_4$-based DRA prototype is designed using the microstrip-slot coupling scheme. Figure 7 demonstrates the configuration of the proposed DRA, and the dimensions are listed in Table 2. A $40 \times 40 \times 1$ mm FR4 substrate is pasted with copper foil (thickness: $\sim 0.06$ mm) on one side as conducting ground plane. A cylindrical CoAl$_2$O$_4$-based dielectric resonator (DR) with a diameter of 9.5 mm and height of 4.8 mm is placed over an etch slot in the
The fields of the microstrip line “leak” through the slot to excite the DR.

Figure 8 shows the simulated antenna performances of the CoAl$_2$O$_4$-based DRA. The $S_{11}$ parameter is a measure of impedance mismatch and reflects how much power is reflected from the antenna. The minimum $S_{11}$ parameter is generally achieved at the resonant frequency. Meanwhile, for practical applications, the $S_{11}$ values should be lower than $-10$ dB in the whole operating frequency range [36, 37]. As shown in Fig. 8a, the designed DRA resonates at the $Ku$-band region, where an excellent $S_{11}$ of $-40.9$ dB is obtained at the resonant frequency of 14.33 GHz. Besides, a considerably large impedance bandwidth (the frequency range where $S_{11}$ is below $-10$ dB) of 940 MHz is also achieved, which surpasses those reported in microstrip patch antennas [1, 2, 38]. The voltage standing wave ratio (VSWR) is another indicator of impedance mismatch. The VSWR value at the resonant frequency should be close to unity for proper working [37]. As shown in Fig. 8b, the designed DRA exhibits an excellent VSWR of 1.03 at 14.33 GHz and is found to be less than 2 in the entire impedance bandwidth frequency range. Figure 8c shows the total efficiency of the DRA as a function of frequency, where a maximum value of 96.6% is obtained at the resonant frequency. The superior total efficiency surpasses the commercial antenna products (typically ranges from 20% to 70%) and indicates extensive application prospects [38, 39]. Finally, antenna gain is another critical parameter measuring the power radiated in a particular direction. Figure 8d demonstrates the three-dimensional (3D) polar plot of the radiation pattern, and the maximum gain is found to be 5.42 dB. A comparative table on the antenna performances is presented in Table 3. The comparative data suggests that the CoAl$_2$O$_4$-based DRA exhibits superior antenna properties, including $S_{11}$ parameters, bandwidth, and total efficiency, compared to the reported work.

### Table 2 The dimensions of the designed rectangular DRA

| Parameter name     | Parameter | Value (mm) |
|--------------------|-----------|------------|
| DRA-diameter       | D         | 9.5        |
| DRA-height         | H         | 4.8        |
| Substrate-length   | L         | 40         |
| Substrate-height   | h         | 1          |
| Slot length        | $l_s$     | 5.2        |
| Slot width         | $w_s$     | 1.7        |
| Microstrip line width | $w$ | 1.8        |
| GP side width      | $l_m$     | 4          |

4 Conclusions

In this study, single-phase CoAl$_2$O$_4$ ceramics have been successfully prepared via a standard solid-state reaction method. XRD and Raman results demonstrate that CoAl$_2$O$_4$ crystallizes in a largely normal spinel structure with a space group of $Fd-3m$. The SEM images show an ever-optimizing microstructure with the increasing sintering temperature, which is beneficial to the improvement of $\varepsilon_r$ and $Q_f$ values. The optimal microwave dielectric properties ($\varepsilon_r = 9.34$, $Q_f = 30,500$ GHz, and $\tau_f = -54$ ppm/°C) are achieved when sintered at 1550 °C. A dielectric resonator antenna is designed using CoAl$_2$O$_4$ ceramics as the antenna element. The outstanding $S_{11}$ ($-40.9$ dB) and VSWR (1.03) values at the resonant frequency of 14.33 GHz indicate a good impedance matching. Moreover, the $S_{11}$ curve exhibits a large impedance bandwidth of 950 MHz, and the total
efficiency at the resonant frequency is 96.6%. The excellent antenna performance suggests that CoAl₂O₄ ceramics have prospects of extensive applications in wireless communication devices operating at the Ku-band, provided \( \tau_f \) can be further tuned toward zero.

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Declarations

Conflict of interest The authors declare no conflicts of interest.
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