



Cold sintered CaTiO_3 - K_2MoO_4 microwave dielectric ceramics for integrated microstrip patch antennas

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ABSTRACT

CaTiO_3 - K_2MoO_4 (CTO-KMO) dielectric composites were successfully cold-sintered at 150 °C for 30 min with a uniaxial pressure of 200 MPa. X-ray diffraction, Raman spectroscopy, back-scattered SEM and energy dispersive x-ray mapping confirmed the coexistence of CTO and KMO with no evidence of interdiffusion and parasitic phases either between the two ceramic end-members or with Ag internal electrodes. As KMO concentration increased, the temperature coefficient of resonant frequency (TCF) and relative permittivity (ϵ_r) decreased but the microwave quality factor ($Q \times f$) increased. A near-zero TCF composition was obtained for CTO-0.92KMO composites which exhibited $\epsilon_r \sim 8.5$ and $Q \times f \sim 11,000$ GHz. A microstrip patch antenna was designed and fabricated using cold sintered CTO-0.92KMO as a substrate ($40 \times 40 \times 1.4$ mm), which gave a S_{11} of -14.2 dB and a radiation efficiency of 62.0 % at 2.51 GHz.

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1. Introduction

Fifth generation (5 G) cellular network technology provides far faster and more reliable broadband access, with greater capacity and lower response times. New microwave (MW) materials are however, required to maximise the use of frequency ranges that have been made available for 5 G. 5 G requires components with lower power consumption (dielectric loss < 0.001), shorter delay times (latency, $t_{pd} < 1$ ms as opposed to < 25 ms) and greater functionality than their 4 G counterparts [1–5]. Latency depends on the relative permittivity (ϵ_r) of ceramics, according to:

$$t_{pd} = \frac{\ell \sqrt{\epsilon_r}}{c}, \quad (1)$$

where ℓ = transmission distance, c = speed of light in vacuum. Therefore, antennas, resonators, filters, substrates and microstrip lines in 5 G communication devices will require low dielectric loss, low ϵ_r (< 15) materials, such as alumina, silicates, molybdates,

borates and tungstates [6–14]. However, ceramics are manufactured using conventional sintering technology (> 1000 °C) and thus cannot be directly integrated into polymer circuit boards (PCBs). Therefore, to truly create a revolution in RF component manufacture for 5 G technology, integrated ceramic components are required which densify at temperatures less than that of the melting point of polymers (typically < 200 °C). Until recently, this was considered impossible but cold sintering, emerging from the group of Randall and co-workers is capable of densifying MW ceramics and composites at < 200 °C, including Li_2MoO_4 (LMO), MoO_3 , $\text{Na}_2\text{Mo}_2\text{O}_7$ (NMO), $\text{K}_2\text{Mo}_2\text{O}_7$, $(\text{LiBi})_{0.5}\text{MoO}_4$, LMO-PTFE, Al_2SiO_5 -NaCl, and LMO- $\text{BaFe}_{12}\text{O}_{19}$ [15–30]. Recent work has demonstrated that low temperature coefficient of resonant frequency (TCF) ($< \pm 10$ ppm/°C) and ϵ_r ($17 < \epsilon_r < 50$) is achieved in cold-sintered LMO- $\text{Na}_{0.5}\text{Bi}_{0.5}\text{MoO}_4$ and NMO ($\text{Bi}_{0.95}\text{Li}_{0.05}$)($\text{V}_{0.9}\text{Mo}_{0.1}$) O_4 dielectric composite ceramics [31–33] but, to date, no reported cold-sintered MW materials with near-zero TCF meet the requirements of 5 G technology, i.e. low ϵ_r and low dielectric loss ($\tan \delta$, high quality factor $Q \times f$). In the present work, end-members, CaTiO_3 (CTO, $\epsilon_r = 160$, TCF = $+850$ ppm/°C) [34] and K_2MoO_4 (KMO, $\epsilon_r = 6.37$, TCF = -70 ppm/°C) [32], were selected to prepare a series of ceramic composites with the prospect for producing a low ϵ_r (< 15), near-zero TCF and high $Q \times f$ material suitable for 5 G antenna substrates.

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2. Experimental section

To prepare (1-x)CTO-xKMO (x = 0.2, 0.5, 0.7, 0.8, 0.92, 1 in weight) composite ceramics, commercial CTO (Alfa Aesar, > 99 %) and KMO (Alfa Aesar, > 95 %) powder were mixed with a small amount of deionized water (5–10 wt%). The mixtures were hot-pressed 30 min at 150 °C and 200 MPa and dried 24 h at 120 °C to remove any remaining moisture. The bulk density of sintered pellets was calculated by a geometric method. The microstructure, crystal structure and phase assemblage was revealed by FEI Inspect F-50 scanning electron microscopy (SEM), Bruker D2 Phaser X-ray powder diffraction (XRD) and Renishaw inVia Raman spectroscopy, respectively. The TE_{01δ} dielectric resonator method was used to measure ϵ_r , TCF, $\tan\delta$ and $Q \times f$, in conjunction with an Advantest R3767CH vector network analyzer (Tokyo, Japan). To determine TCF, the resonant frequency (f) was measured in a heated cavity by a Peltier device in a temperature range of 25 °C ~ 85 °C, and then inputted into Eq. (2).

$$\text{TCF} = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \quad (2)$$

where the f_T and f_{T_0} were f at temperatures of T and T_0 , respectively.

3. Results and discussion

Relative densities (ρ_r) of cold-sintered CTO-xKMO ceramic composites are listed in Table 1, which increased from 89 % for CTO-0.2KMO to 100 % for compositions with $x > 0.5$.

Room-temperature XRD patterns and Raman spectra of commercial CTO powder and cold-sintered CTO-xKMO samples are

Table 1

Relative densities (ρ_r), and microwave dielectric properties of CTO-KMO ceramics.

Composition	ρ_r (%)	ϵ_r	$\tan\delta$	$Q \times f$ (GHz)	TCF (ppm/°C)
CTO-0.2KMO	89	46.6	0.004	1000	+317
CTO-0.5KMO	97	37.2	0.004	1030	+274
CTO-0.7KMO	100	20.9	0.001	4360	+142
CTO-0.8KMO	100	13.7	0.0008	7170	+70
CTO-0.92KMO	100	8.5	0.0008	11000	-4
KMO	100	6.4	0.0003	26470	-70

shown in Fig. 1. CTO and KMO exhibit a perovskite orthorhombic (space group: $Pnma$, PDF card: 42-423) and a monoclinic structure (space group: $C12/m1$, PDF card: 29-1021), respectively. All diffraction peaks in the XRD patterns for CTO-xKMO are assigned to either CTO and KMO and the reflection intensities of KMO increase with increasing weight fraction, as labelled in Fig. 1(a). Coexistence of diffraction peaks related to CTO and KMO is found in all studied composites with $0 < x < 1$, with no trace of impurity peaks or shift of peak positions, indicating that there is no detectable interaction between CTO and KMO. To confirm the weight fraction of each end member in the composites, full-pattern Rietveld refinement of X-ray data was conducted using a two phase mix of CTO ($Pnma$) and KMO ($C12/m1$) with CTO-0.2KMO and CTO-0.8KMO given in Fig. 1(c) and (d), respectively. Good agreement is observed between the experimental and calculated patterns with weight fractions close to the nominal compositions.

For orthorhombic ($Pnma$) CTO, a total of 117 vibrational modes are expected (24 Raman-active modes) according to previous reports [35–37]. However, most of these bands cannot be observed due to their low change in polarizability. Instead, ten main Raman

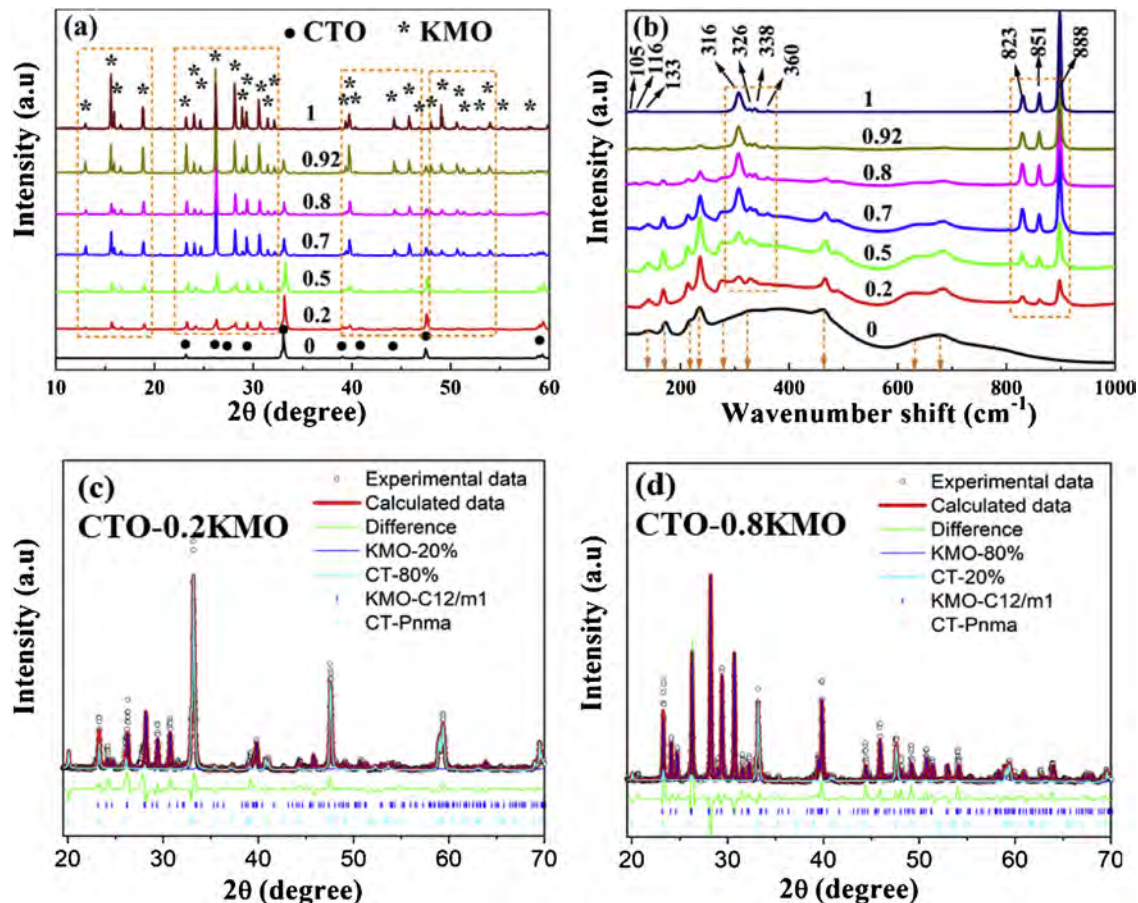


Fig. 1. Room-temperature (a) XRD patterns and (b) Raman spectra of CTO-xKMO composite ceramics.

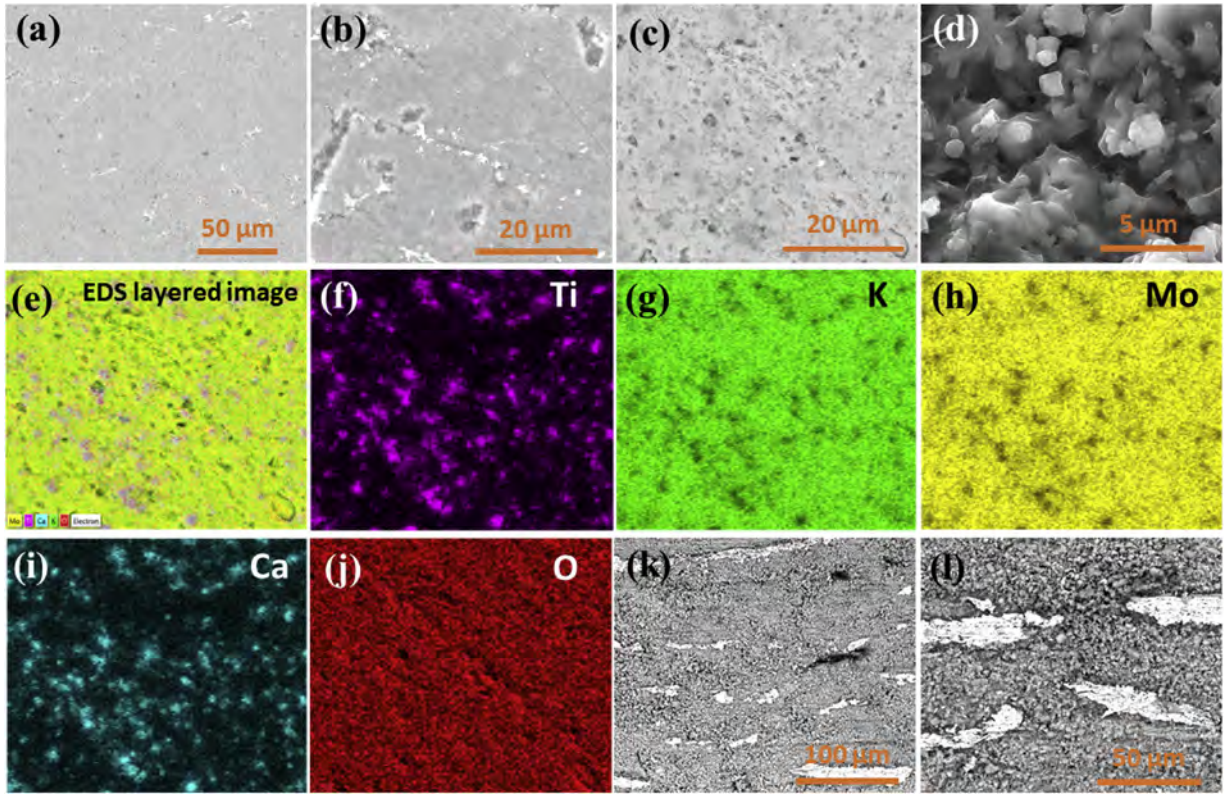


Fig. 2. The BSE images of cold-sintered (a) CTO-0.2KMO, (b) CTO-0.5KMO, and (c) CTO-0.92KMO polished surfaces. (d) The SEM image of cold-sintered CTO-20 %KMO fracture surface. EDS elemental mapping results of polished CTO-0.92KMO samples: (e) elemental layered image, (f) Ti, (g) K, (h) Mo, (i) Ca, (j) O. (k,l) The BSE images of cold-sintered CTO-0.92KMO with Ag paste.

bands are observed for CTO at 140, 172, 220, 235, 275, 323, 463, 492, 630 and 678 cm^{-1} , which are assigned to the Ti–O symmetric stretching (630, 678 cm^{-1}), Ti–O torsional mode (bending or internal vibration of oxygen cage, 463, 492 cm^{-1}), O–Ti–O bending (172, 220, 235, 275, 323 cm^{-1}) and motion of A-site ions (140 cm^{-1}). Based on the group theory together with irreducible representations, 39 vibrational modes are found in KMO, [38,39], given as follows:

$$\Gamma_{\text{KMO}} = 13A_g + 7A_u + 8B_g + 11B_u \quad (3)$$

18 modes of $6A_g + 3A_u + 3B_g + 6B_u$ are assigned to the internal modes of MoO_4 tetrahedra, where the stretching modes are distributed as $2\nu_1 (A_g + B_u)$ and $6\nu_3 (2A_g + A_u + B_g + 2B_u)$ and the bending modes are distributed as follows $4\nu_2 (A_g + A_u + B_g + B_u)$ and $6\nu_4 (2A_g + A_u + B_g + 2B_u)$. The remaining lattice modes are related to the translations of the potassium ions ($4A_g + 2A_u + 2B_g + 4B_u$), vibrations of the MoO_4 tetrahedra ($A_g + 2A_u + 2B_g + B_u$) and translations of the MoO_4 tetrahedra ($2A_g + A_u + B_g + 2B_g$). Only the superimpose of spectral bands is observed in Raman spectra of CTO–KMO composites, related to each individual phase, verifying the presence of CTO and KMO in ceramic composites (Fig. 1a,b) but with no interdiffusion. Moreover, the intensities of KMO Raman modes are found to increase gradually with increase in KMO concentration.

Back-scattered electron (BSE) images of polished surfaces for cold-sintered CTO–xKMO are shown in Fig. 2(a–c). Microstructures appear dense in all studied ceramic composites (also observed in fracture surface of CTO–BMO, Fig. 2d), in agreement with data given in Table 1. Image contrast indicates that the microstructure is composed of two chemically discrete and distinct phases which are identified by EDS mapping (Fig. 2e–j) as KMO (light contrast) and CTO (dark contrast), respectively, consistent with XRD patterns and Raman spectra (Fig. 1). To check the compatibility of CTO–xKMO

composite ceramics with Ag electrodes, Ag paste was introduced in the cold-sintered CTO-0.92KMO composite ceramics, with BSE images shown in Fig. 2(k,l). The bright regions correspond to Ag due to its greater weight averaged atomic number than CTO-0.92KMO with no evidence of reaction at the ceramic/electrode interface, indicating good compatibility.

The microwave dielectric properties of CTO–xKMO composite ceramics as a function of weight fraction (x) KMO are presented in Fig. 3 and listed in Table 1. ϵ_r and TCF decrease linearly from 46.6 and +317 ppm/°C, respectively, for CTO-0.2KMO to 6.4 and -70 ppm/°C for KMO. $Q \times f$ increases from 1000 GHz for CTO-0.2KMO to 26470 GHz for KMO, as shown in Fig. 3 and Table 1. A near-zero TCF (-4 ppm/°C) is achieved for CTO-0.92KMO with a low $\epsilon_r \sim 8.5$ and $Q \times f \sim 11,000$ GHz. Assuming no chemical interactions between the respective phases, the effective ϵ_r of composites may be predicted by mixing laws (Eqs. 4–6) [31,32],

$$\text{serieslaw}, 1/\epsilon = V_1/\epsilon_1 + V_2/\epsilon_2 \quad (4)$$

$$\text{parallellaw}, \epsilon = V_1 \times \epsilon_1 + V_2 \times \epsilon_2 \quad (5)$$

$$\text{logarithmic law}, \epsilon = \epsilon_1^{V_1} \epsilon_2^{V_2} \text{ i.e. } \lg \epsilon = V_1 \lg \epsilon_1 + V_2 \lg \epsilon_2 \quad (6)$$

where ϵ_1 and V_1 is the ϵ_r and volume fraction (V) of phase 1, ϵ_2 and V_2 is the ϵ_r and V of phase 2 ($V_1 + V_2 = 1$). In Fig. 3, ϵ_r of CTO–KMO is close to the values calculated using Eq. (6), following a logarithmic mixing law with the respective weight fraction. TCF and $Q \times f$ of composites can be predicted by using a parallel and series mixing rule, respectively

$$\text{TCF} = V_1 \times \text{TCF}_1 + V_2 \times \text{TCF}_2 \quad (7)$$

$$1/(Q \times f) = V_1/(Q_1 \times f_1) + V_2/(Q_2 \times f_2) \quad (8)$$

where TCF_1 , $Q_1 \times f_1$ and TCF_2 , $Q_2 \times f_2$ correspond to the TCF and $Q \times f$ values of phase 1 and phase 2, respectively, Fig. 3(b).

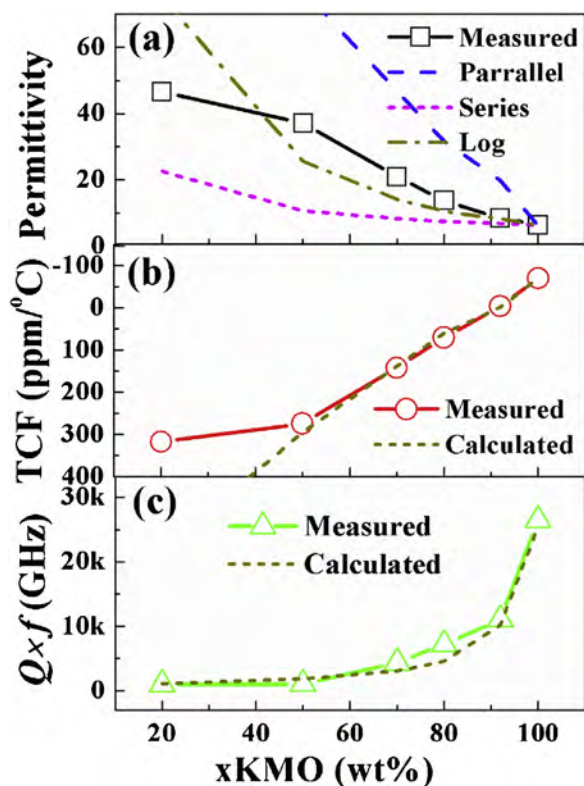


Fig. 3. The microwave dielectric properties (a) ϵ_r , (b) TCF and (c) $Q \times f$ of CTO-xKMO composite ceramics as a function of x (KMO fraction).

Microstrip patch antennas are common RF components that have the advantages of low cost, low profile and easy fabrication, which makes them popular for consumer wireless devices such as mobile phones and tablets. A microstrip patch antenna consists of a top radiation element and a bottom ground plane, separated by a dielectric substrate. The dielectric substrate plays an important role to optimise antenna performance such as bandwidth and antenna efficiency.

A rectangular microstrip patch antenna was fabricated from $40.0 \text{ mm} \times 40.0 \text{ mm} \times 1.4 \text{ mm}$ CTO-0.92KMO substrate prepared by cold sintering. The radiation element and ground plane were made from copper tape with a thickness of $\sim 0.05 \text{ mm}$. The radiation element had the dimension of $27.5 \text{ mm} \times 23.0 \text{ mm}$, while the ground plane has the same dimension as the substrate. A coaxial probe feed

was used with a feed point $\sim 6 \text{ mm}$ from the long edge (27.5 mm edge) of the radiation element. The described dimension resulted in a microstrip patch antenna operating at a resonant frequency of $\sim 2.5 \text{ GHz}$. An image of the fabricated microstrip patch antenna is shown in the inset of Fig. 4(a). The measured s_{11} result of the antenna is shown in Fig. 4(a). It shows the impedance of the antenna is well matched with $s_{11} = -14.2 \text{ dB}$ at 2.51 GHz . The measured radiation pattern on the E-plane (the electric field vector, normal to the electric plane) and the H-plane (the magnetic field vector, normal to the electric plane) of the antenna are shown in Fig. 4(b). The realised gain of this antenna at 2.5 GHz was 2.73 dB , which led to a radiation efficiency of 62.0% . The low sintering temperature of the ceramic (150°C) and the excellent antenna performance confirm the potential of directly fabricating antenna substrates onto metallised PCBs for future integrated 5 G antenna applications.

4. Conclusions

Cold sintered CTO-KMO microwave composite ceramics with $89\% - 100\%$ relative density were fabricated at 150°C and a uniaxial pressure of 200 MPa for a hold time of 30 min . Only CTO and KMO phases were present in composite ceramics and there was no evidence of chemical reaction between the two phases by XRD, SEM and Raman spectroscopy. Ag paste was introduced in cold-sintered CTO-0.92KMO samples, and BSE images indicated no evidence of reaction at the interface between ceramic and electrode, suggesting good compatibility for the future fabrication of more complex integrated devices. As the weight fraction of KMO increased, ϵ_r and TCF decreased and $Q \times f$ increased. A near-zero TCF of $+4 \text{ ppm}/^\circ\text{C}$ was obtained in CTO-0.2KMO with $\epsilon_r \sim 8.5$ and $Q \times f \sim 11,000 \text{ GHz}$. A microstrip patch antenna was designed and fabricated using cold sintered CTO-0.2KMO as a substrate which operated at 2.51 GHz with a radiation efficiency of 62.0% . Cold sintered CTO-KMO is therefore, considered to have great potential for the fabrication of integrated devices, directly fabricated on metallised PCBs for 5 G applications.

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.

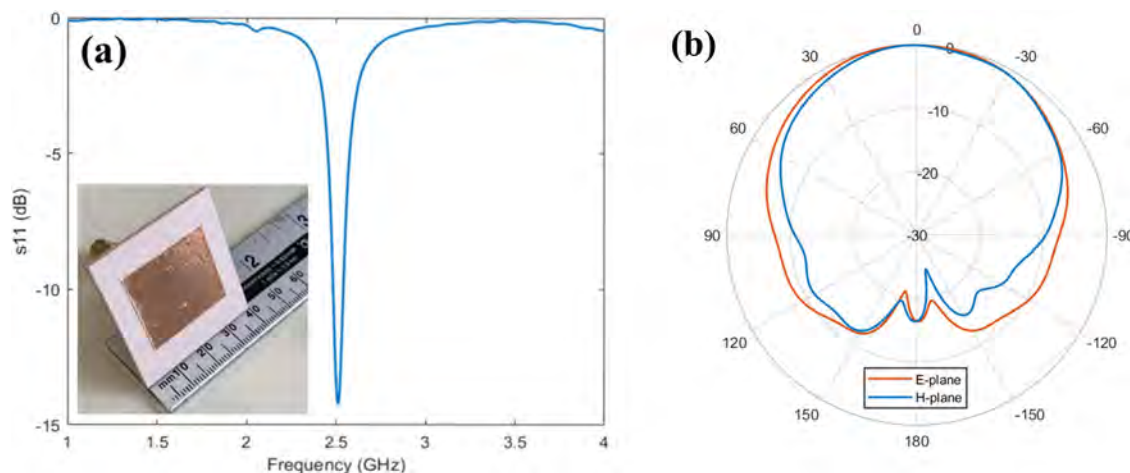


Fig. 4. Measured (a) s_{11} , and (b) radiation pattern of the CTO-0.92KMO microstrip antenna. The picture of fabricated microstrip antenna is given in the inset of (a).

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