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# Direct Integration of Cold Sintered, Temperature-Stable Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub>-K<sub>2</sub>MoO<sub>4</sub> Ceramics on Printed Circuit Boards for Satellite Navigation

## Antennas

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## ABSTRACT

Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub>-K<sub>2</sub>MoO<sub>4</sub> (BMO-KMO) composite ceramics with >95% theoretical density were densified by cold sintering at 150 °C. XRD, Raman, back-scattered SEM and EDX spectroscopy indicated that the BMO and KMO phases coexisted in all composites without inter-diffusion and secondary phases. Temperature coefficient of resonant frequency with near-zero value ~ -1 ppm/°C was achieved for BMO-10%KMO with permittivity ~ 31 and quality factor ~ 3,000 GHz. Cold-sintered composite ceramics were directly pressed/integrated onto a printed circuit board (PCB) using the Cu metallisation as a ground plane for the design and fabrication of a circularly polarized microstrip patch antenna suitable for satellite navigation systems which achieved efficiencies 87% at 1561 MHz (BeiDou) and 88% at 1575 MHz (GPS/Galileo). The low cost, low energy integration of temperature stable, cold sintered ceramics directly onto a PCB represents a step change in substrate fabrication technology for RF devices.

**Keywords:** microwave dielectric ceramics; cold sintering process; microstrip patch antennas

## 1. Introduction

Microwave (MW) ceramics are widely used in modern wireless communication systems as resonators, couplers, filters, substrates and capacitors.[1] However, conventional ceramic sintering technology at  $>1000$  °C is commonly used to densify ceramics. [2-5] Low-temperature co-fired ceramics (LTCC, 700-900 °C sintering temperature) and ultra-low temperature co-fired ceramics (ULTCC, 400-600 °C sintering temperature) can be co-sintered with low cost electrodes (Ag, Cu and Al, etc.). [6-15] To date, temperature-stable MW ceramics cannot be directly integrated onto polymer-based printed circuit boards (PCBs) in a single deposition step from powder. To revolutionize radio frequency (RF) manufacturing therefore, low loss (high quality factor,  $Qf \geq 3000$  GHz), temperature-stable (low temperature coefficient of resonant frequency,  $TCF = \pm 3$  ppm/°C), medium permittivity ( $8 < \epsilon_r < 40$ ) are required that densify at  $<200$  °C and permit printing/pressing directly onto PCBs, reducing the costs and energy used in manufacturing and increasing functionality.

The cold sintering process (CSP) can densify materials and devices at  $< 200$  °C and exhibits great potential for developing novel RF technology and manufacturing processes. Numerous articles have recently appeared on a wide range of materials such as  $\text{Li}_2\text{MoO}_4$  (LMO),  $\text{MoO}_3$ ,  $\text{Na}_2\text{Mo}_2\text{O}_7$  (NMO),  $\text{K}_2\text{Mo}_2\text{O}_7$ ,  $(\text{LiBi})_{0.5}\text{MoO}_4$ , LMO-PTFE,  $\text{Al}_2\text{SiO}_5\text{-NaCl}$ , LMO- $\text{Mg}_2\text{SiO}_4$  and LMO- $\text{BaFe}_{12}\text{O}_{19}$ . [16-31], including a range of temperature stable low loss composites by the present authors,  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{MoO}_4\text{-LMO}$ ,  $(\text{Bi}_{0.95}\text{Li}_{0.05})(\text{V}_{0.9}\text{Mo}_{0.1})\text{O}_4\text{-NMO}$  and  $\text{CaTiO}_3\text{-KMO}$  with  $8 < \epsilon_r < 40$ . [32-34] Furthermore, standalone RF devices such as temperature stable COG multilayer ceramic capacitors (MLCCs) and microstrip patch antennas have been fabricated. [34, 35] However, the ‘*holy grail*’ of cold-sintered MW ceramics directly pressed/integrated onto PCBs followed by device design and fabrication, has not to date been demonstrated. In this work,  $\text{Bi}_2\text{Mo}_2\text{O}_9$  (BMO,  $\epsilon_r = 38$ ,  $TCF = +31$  ppm/°C,  $Q \times f = 12,500$ ) [15, 36-38] and KMO ( $\epsilon_r = 6.4$ ,  $TCF = -70$  ppm/°C,  $Q \times f = 26,500$ ) [33, 34] were selected with the intent of fabricating MW

composite ceramics with near-zero TCF. Direct integration of these ceramics onto PCBs is demonstrated followed by the simulation and fabrication of a microstrip patch antenna suitable for satellite navigation systems.

## 2. Experimental

(1-x)BMO-xKMO (x = 5wt%, 10wt%, 20wt%, 50wt%, 100wt%) composite ceramics were prepared by CSP. BMO powder was synthesised by the solid-state reaction method. Raw chemicals Bi<sub>2</sub>O<sub>3</sub> (99.9%, Acros Organics) and MoO<sub>3</sub> (>99%, Acros Organics) were weighed with a Bi<sub>2</sub>O<sub>3</sub>: MoO<sub>3</sub> ratio of 1:2 and ball-milled 4 h in solvent isopropanol. The mixed powders were dried, calcined 4 h at 630-650°C to synthesize the compound and ball-milled 4 h in isopropanol to reduce particle size. [15, 36-38] KMO (Alfa Aesar, > 95%) and BMO powders were mixed with 5-10 wt% deionized water, hot-pressed 30 min at 150 °C and 600 MPa (Atlas Heated Platens, Specac) and dried 24 h at 120 °C to remove residual moisture. BMO ceramics were conventionally sintered at 680 °C for 2h.

The densities of ceramic samples were measured by a geometric method.[17-34] Crystal structure, phase assemblage and microstructure were determined by Bruker D2 Phaser X-ray powder diffraction (XRD, CuK $\alpha$  radiation), Renishaw inVia Raman microscope Raman spectroscopy and an FEI Inspect F-50 scanning electron microscopy (SEM). The TE<sub>01 $\delta$</sub>  mode was employed to measure the microwave dielectric properties of ceramics using an Advantest R3767CH vector network analyzer. The cavity was heated by a Peltier device and the resonant frequency ( $f$ ) was measured from 25 °C to 85 °C. The corresponding TCF values were obtained using the formula:

$$\text{TCF} = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \quad (1)$$

where the  $f_T$  and  $f_{T_0}$  are the TE<sub>01 $\delta$</sub>  resonant frequencies at temperatures, T and T<sub>0</sub>, respectively.

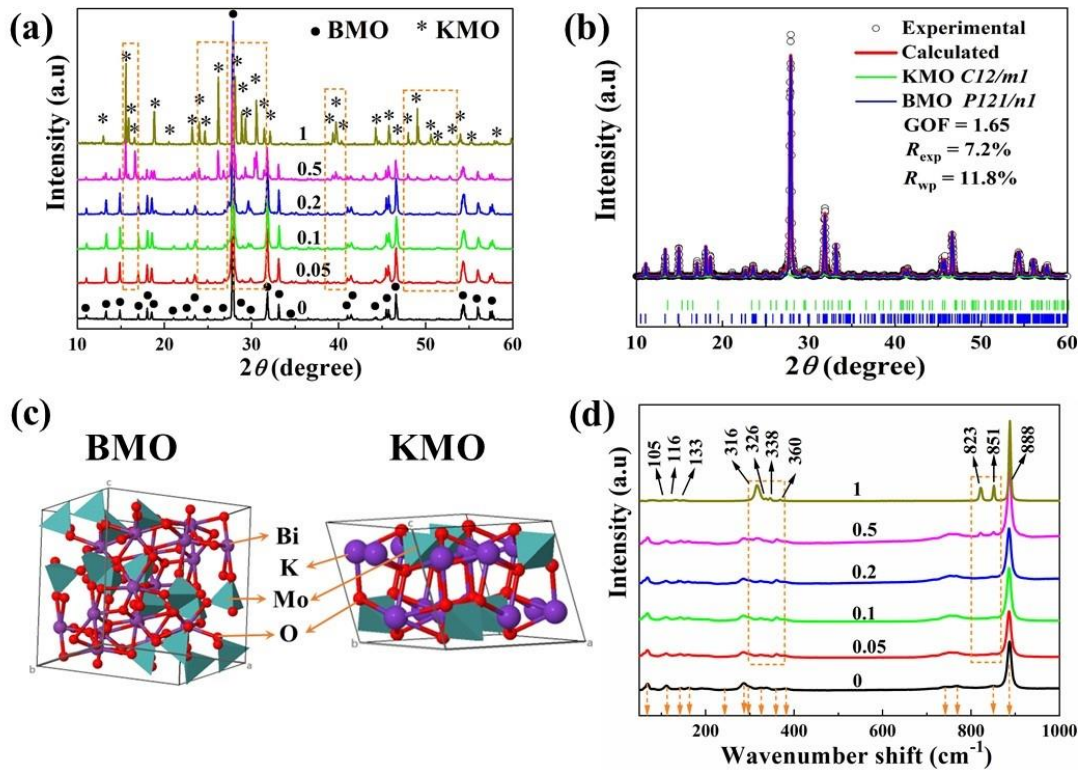
### 3. Results and discussion

The relative density ( $\rho_r$ ) of cold-sintered BMO-xKMO composites increases from 90% for BMO-5%KMO to 100% for  $x > 0.05$ , Table I, confirming that dense BMO-xKMO composites are readily fabricated by cold sintering.

**Table I.** Sintering temperature (ST), relative density ( $\rho_r$ ), and microwave dielectric properties of BMO-KMO ceramics.

Composition	ST (°C)	$\rho_r$ (%)	$\epsilon_r$	$\tan\delta$	$Q \times f$ (GHz)	TCF (ppm/°C)
BMO	680	95±1.8	38	0.0004	11000	+31
BMO-5%KMO	150	87.3±2.3	28	0.001	4700	+17
BMO-10%KMO	150	99.6±1.9	31	0.002	3000	-1
BMO-20%KMO	150	100±0.6	27	0.004	1600	-31
BMO-50%KMO	150	100±1.1	22	0.006	1300	-55
KMO	150	100±1.5	6.4	0.0003	26500	-70

The XRD patterns of cold-sintered BMO-xKMO ceramics are given in Fig. 1(a). Both BMO and KMO are monoclinic with  $P121/m1$  (ICSD: 201742) and  $C12/m1$  (ICSD: 16154) symmetry, respectively.[15, 33, 34, 36-38] B-site  $\text{Mo}^{6+}$  cations are coordinated by four O-anions, leading to tightly bound  $\text{MoO}_4$  tetrahedra. The A-site  $\text{Bi}^{3+}$  or  $\text{K}^+$  cations are circled by eight or six O anions, as displayed in the schematic crystal structures of BMO and KMO (Fig. 1c). Diffraction peaks in the XRD patterns of BMO-xKMO composites may all be ascribed to either BMO and KMO. The diffraction peak intensity of KMO increases with the weight fraction of KMO increasing, as marked in Fig. 1(a) but no impurity peaks, nor shift in peak position are observed.



**Figure 1.** (a) XRD patterns of BMO-xKMO ceramic composites. (b) Rietveld refinement of BMO-10%KMO. The schematic crystal structures of (c) BMO and KMO. (d) Raman spectra of BMO-xKMO ceramic composites

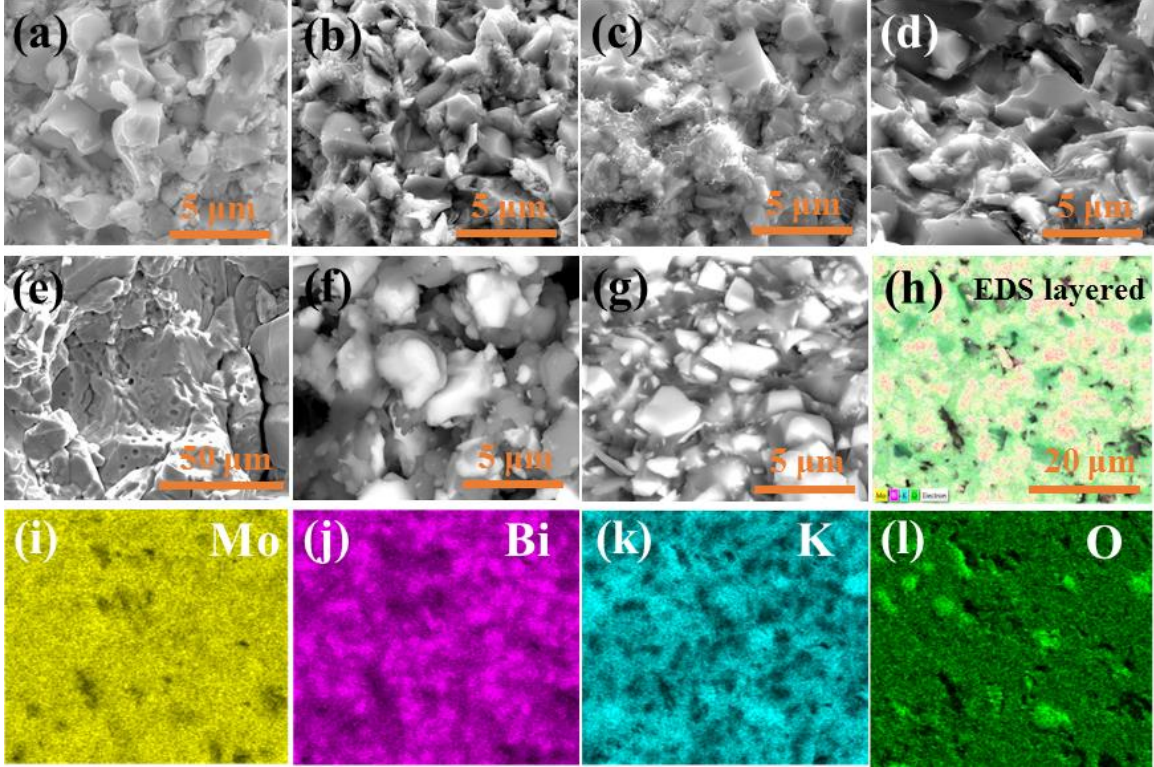
To further evaluate the phase composition and lattice parameters of BMO-KMO, full-pattern Rietveld refinement of BMO-10%LMO was performed using a Topas 5 software, where a two-phase refinement ( $C12/m1 + P121/n1$ ) is used. Low values of  $GOF = 1.65$ ,  $R_{exp} = 7.2\%$  and  $R_{wp} = 11.8\%$  indicate that the calculated result agrees with the observed pattern, Fig. 1(b). The weight fraction of BMO ( $C12/m1$ , 89%) and KMO ( $P121/n1$ , 11%) phases is determined for BMO-10%KMO, close to the nominal composition. The calculated lattice parameters are  $a = 11.9515 \text{ \AA}$ ,  $b = 10.8007 \text{ \AA}$ ,  $c = 11.8814 \text{ \AA}$  for BMO and  $a = 12.672 \text{ \AA}$ ,  $b = 6.030 \text{ \AA}$ ,  $c = 7.066 \text{ \AA}$  for KMO, respectively, which agree with the reported values. [15, 33, 34, 36-38]

The room-temperature Raman data of BMO-xKMO composites is shown in Fig. 1(d). In agreement with previous reports, [39, 40] 14 Raman bands are observed in the spectrum of BMO at 68, 114, 142, 176, 260, 284, 296, 321, 358, 380, 739, 768, 851 and 888  $\text{cm}^{-1}$ , which were assigned to bending ( $260 \sim 380 \text{ cm}^{-1}$ ) and stretching ( $739 \sim 888 \text{ cm}^{-1}$ ) modes of  $\text{MoO}_4$  tetrahedra and the conversion of Mo/Bi atoms ( $< 260 \text{ cm}^{-1}$ ), respectively. According to group theory, there are 39 different vibrational modes in KMO,[41, 42]:

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

The Raman bands in the range of  $100 \sim 160 \text{ cm}^{-1}$  correspond to a combination of the translations and vibrations of  $\text{MoO}_4$  tetrahedra and translations of K ions. The  $310 \sim 370 \text{ cm}^{-1}$  bands are related to bending modes of  $\text{MoO}_4$  tetrahedra. The  $820 \sim 890 \text{ cm}^{-1}$  bands are related to stretching modes of  $\text{MoO}_4$  tetrahedra. Raman spectra of BMO-KMO composites therefore, constitute an overlay of Raman bands from individual phases (Fig. 1d). The intensity of Raman modes for KMO increase gradually with increase in x.

SEM images of the cross-section for the cold-sintered BMO-KMO samples are given in Fig. 2(a-e). All compositions with  $x > 0.05$  have dense microstructures, in agreement with measured densities in Table I. The dark and light regions of contrast in BSE images of mixed BMO-KMO powder (Fig. 2f) and cold-sintered BMO-50%KMO (Fig. 2g) suggest that two chemically distinct KMO and BMO rich phases are present which is confirmed by EDS mapping (Fig. 2h-l) and in agreement with Raman spectra and XRD patterns (Fig. 1).



**Figure 2.** SEM images of the cross-section for cold-sintered BMO-xKMO (a) 5%, (b) 10%, (c) 20%, (d) 50%, (e) 100%. BSE images of (f) mixed BMO and KMO powder, (g) cold-sintered BMO-50%KMO cross-section. EDS mapping images of cold-sintered BMO-50%KMO samples: (h) elemental layered image, (i) Mo, (j) Bi, (k) K, (l) O.

Fig. 3 shows the microwave dielectric properties of BMO-xKMO ceramic composites with increase of KMO weight fraction, Table I.  $\epsilon_r$  and TCF linearly decrease from 39 and +31 ppm/°C, to 6.4 and -70 ppm/°C, respectively.  $Qf$  of BMO-xKMO composites ceramics is lower than both end members and in the range of 1300~4700, likely due to residual amorphous phase in cold-sintered systems.[16-34] Near-zero value of TCF (-1 ppm/°C) is obtained for BMO-10%KMO with  $\epsilon_r \sim 31$  and  $Qf \sim 3,000$  GHz. The effective  $\epsilon_r$  can be calculated by the following mixing laws:[32-34]

$$\text{parallel law, } \epsilon = V_1 \epsilon_1 + V_2 \epsilon_2 \quad (4)$$

$$\text{series law, } 1/\epsilon = V_1 / \epsilon_1 + V_2 / \epsilon_2 \quad (5)$$

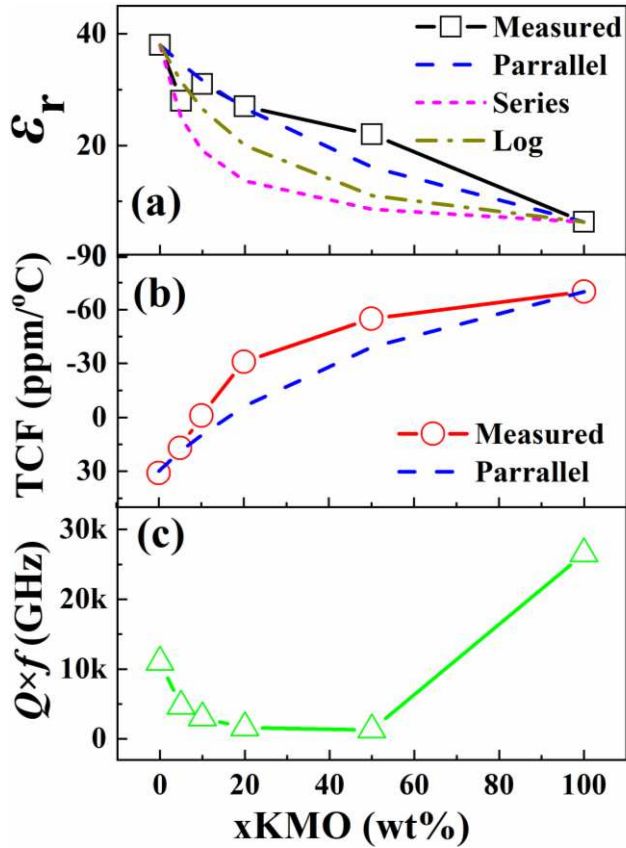


$$\text{logarithmic law, } \varepsilon = \varepsilon_1^{V_1} \varepsilon_2^{V_2} \text{ i.e. } \lg \varepsilon = V_1 \lg \varepsilon_1 + V_2 \lg \varepsilon_2 \quad (6)$$

where  $\varepsilon_1$  is the  $\varepsilon_r$  of phase 1,  $\varepsilon_2$  is the  $\varepsilon_r$  of phase 2,  $V_1$  is the volume fraction of phase 1 and  $V_2$  ( $1 - V_1 = V_2$ ) is the volume fraction of phase 2.  $\varepsilon_r$  follows indicated a parallel mixing law, Fig. 3(a) and 3(b), which may also be used to predict TCF, according to:

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

where  $\text{TCF}_1$  and  $\text{TCF}_2$  are the temperature coefficients of phase 1 and 2, respectively, Fig. 3(b).

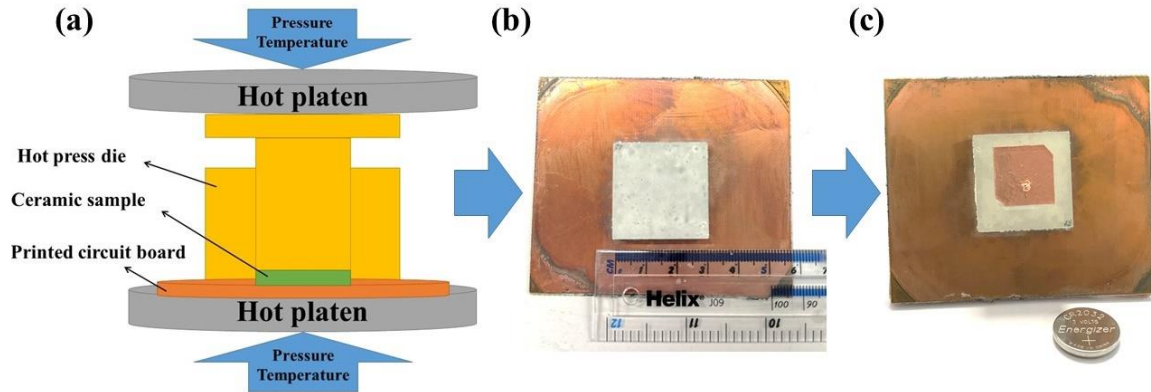


**Figure 3.** Microwave properties of BMO-xKMO composites vs. KMO weight fraction.

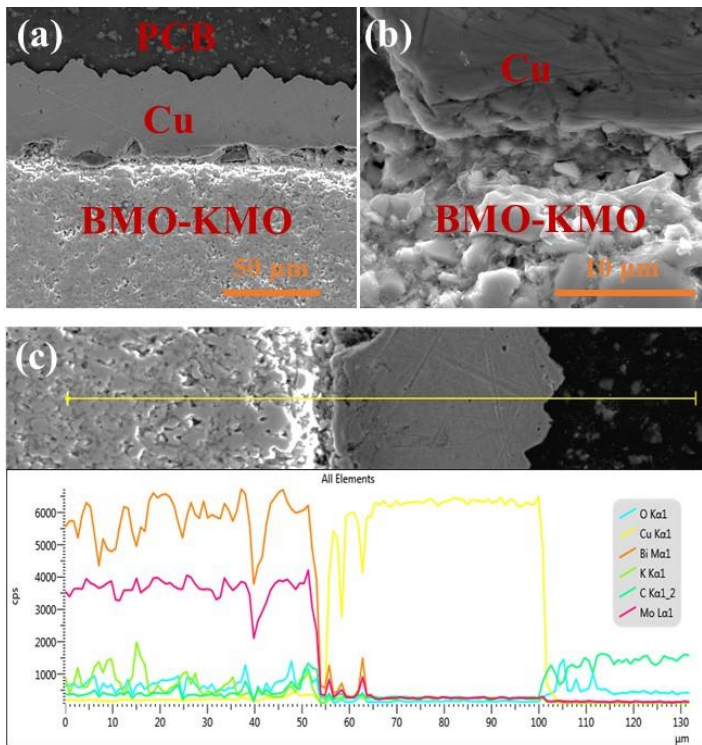
Satellite navigation systems are widely used in consumer electronics and provide navigation, localization, and tracking. The Global Satellite Navigation System (GLONAS), Global Positioning System (GPS), Gallileo and Beidou were installed by Russia, United states, Europe and China, respectively and all operate around 1.5-1.6 GHz. The antenna is one of the key

components to ensure low latency, good reception to provide high precision positioning and robust communication. Microstrip patch antennas are a popular choice in modern electronics due to their low-profile, low-cost, ease of fabrication and their small physical size for integration into limited space. Generally, ceramic dielectrics with overall dimensions of 20 mm × 20 mm × 2 mm to ~ 40 mm × 40 mm × 7 mm have been widely used as the substrates for satellite navigation antennas for vehicles. Satellite navigation antennas are mainly sold as individual units in which the ceramic is sintered at >1200 °C and which require assembling using a ‘pick and place’ procedure. The modular design helps end-users to reduce cost with respect to customization but some highly integrated, direct compact packaged systems require satellite navigation antennas that can be directly fabricated on PCBs. This is impossible with conventionally sintered ceramics (>1200 °C) but cold sintering densifies powders at less than the melting point (<200 °C) of the PCB board and hence can be directly pressed onto its surface and fully integrated from a manufacturing perspective.

In this work, BMO-10%KMO ceramic substrates 30 mm × 30 mm × 7 mm were directly cold-sintered onto an 85 mm × 75 mm × 1.6 mm glass-reinforced epoxy laminate PCB (FR4), as schematically indicated in Fig. 4(a). The Cu layer of the FR4 was intentionally not removed and acted as the ground plane (Fig. 4b). For proof of concept, the top patch was cut from a conductive copper tape with dimensions of 18.5 mm × 18.5 mm and two cut corners to achieve circular polarization but for mass production, it could be screen printed using a low temperature binder-burn out conductive ink. The fabricated antenna is shown in Fig. 4(c). The SEM images and EDS elemental line scans of a cross-section of cold-sintered BMO-10%KMO on PCBs are shown in Fig. 5. A Cu layer of ~ 45 μm thick is shown in the enlarged BSE image, Fig. 5(a,c), which has a sharp interface with the ceramic grains, indicating chemical/temperature compatibility with the BMO-KMO layer, further confirmed from the EDS elemental line-scans, Fig. 5(c).

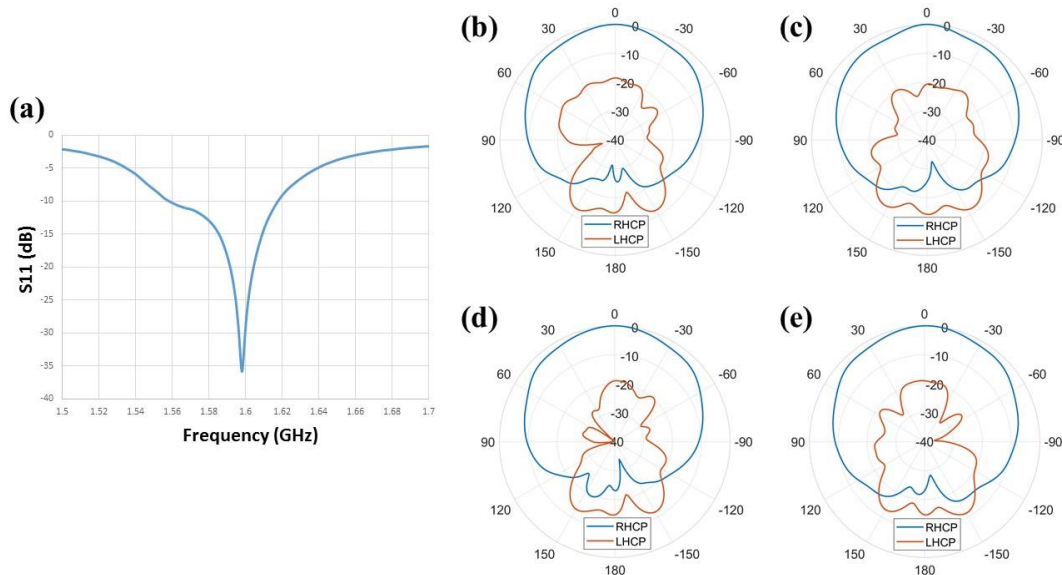


**Figure 4.** (a) The schematic diagram of cold-sintering ceramic substrate for antenna. (b) cold-sintered BMO-10%KMO ceramic substrate with a dimension of 30 mm × 30 mm × 7 mm on an 85 mm × 75 mm × 1.6 mm glass-reinforced epoxy laminate PCB (FR4). (c) The fabricated antenna with cold-sintered BMO-10%KMO ceramic as substrate.



**Figure 5.** (a, b) SEM images (c) EDS elemental line-scans of a cross-section of cold-sintered BMO-10%KMO on a Cu metallised PCB.

The antenna gave a right-hand circular polarization (RHCP) across a wide operating frequency and supported the B1I (1561 MHz) band for BeiDou, L1 (1575 MHz) GPS and E1 (1575 MHz) for Galileo. The measured S11 is shown in Fig. 6(a), indicating that the ceramic microstrip patch antenna is well matched and has -10 dB bandwidth of 59 MHz that covers the desired frequency 1561 MHz and 1575 MHz. The far-field performance of the antenna was measured in an anechoic chamber and the parameters are summarized in Table II. The total antenna efficiencies (include the S11 mismatch) are 87% at 1561 MHz (BeiDou) and 88% at 1575 MHz (GPS/Galileo). The axial ratio was < 3 dB at both frequencies which indicated good circular polarization. The circular polarization performance is particularly important for satellite navigation applications since the relative orientation of the transmitting and receiving antennas is not fixed, and the circularly polarization is able to overcome the Faraday rotation effect due to the ionosphere thereby maximising signal reception. The measured radiation patterns at 1561 MHz and 1575 MHz of the ceramic microstrip antenna are shown in Fig. 6(b-e), respectively.



**Figure. 6.** (a) Measured S11 curve; Measured radiation patterns in Azimuth (b) and Elevation plane (c) at 1561 MHz; Measured radiation patterns in Azimuth (d) and Elevation plane (e) at 1575 MHz.

**Table II.** Measured antenna performance of the fabricated ceramic microstrip patch antenna at two frequency bands.

Parameters	BeiDou	GPS/Galileo
Frequency	1561 MHz	1575 MHz
Polarization	RHCP	RHCP
Gain	5.7 dBic	5.8 dBic
Directivity	6.4 dBic	6.4 dBic
Total efficiency	87%	88%
Axial ratio	2.1 dB	1.9 dB

#### 4. Conclusions

BMO-KMO microwave ceramic composites with high relative densities (90%-100%) were successfully fabricated by cold sintering at 150 °C/30 min/600 MPa. Only BMO and KMO were presented in composites and no chemical reaction occurred between the two end-members, as confirmed by XRD, Raman, BSE and EDS mapping. With increasing weight fraction of KMO,  $\epsilon_r$  and TCF decreased while  $Qf$  increased. TCF  $\sim +1$  ppm/°C was achieved in BMO-10%KMO with  $Qf \sim 3,000$  GHz and  $\epsilon_r \sim 31$ . An antenna for satellite navigation was designed and then fabricated using a BMO-10%KMO substrate (30×30×7 mm) directly pressed onto a PCB metallised circuit board using the Cu layer as a ground plane. The antenna had an S11 of -10 dB with bandwidth of 59 MHz, < 3dB axial ratio that covers the desired frequency bands 1561 MHz and 1575 MHz. The antenna works well at both BeiDou and GPS/Galileo frequencies with efficiencies of 87% at 1561 MHz and 88% at 1575 MHz.

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