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Direct Integration of Cold Sintered, Temperature-Stable Bi₂Mo₂O₉-K₂MoO₄ Ceramics on Printed Circuit Boards for Satellite Navigation Antennas

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ABSTRACT

Bi₂Mo₂O₉-K₂MoO₄ (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 $>1000\text{ }^{\circ}\text{C}$ is commonly used to densify ceramics. [2-5] Low-temperature co-fired ceramics (LTCC, $700\text{-}900\text{ }^{\circ}\text{C}$ sintering temperature) and ultra-low temperature co-fired ceramics (ULTCC, $400\text{-}600\text{ }^{\circ}\text{C}$ 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, $Qf \geq 3000\text{ GHz}$), temperature-stable (low temperature coefficient of resonant frequency, $\text{TCF} = \pm 3\text{ ppm}/^{\circ}\text{C}$), medium permittivity ($8 < \epsilon_r < 40$) are required that densify at $<200\text{ }^{\circ}\text{C}$ 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 $< 200\text{ }^{\circ}\text{C}$ 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 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, $\text{Al}_2\text{SiO}_5\text{-NaCl}$, LMO- Mg_2SiO_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 C0G 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, $\epsilon_r = 38$, $\text{TCF} = +31\text{ ppm}/^{\circ}\text{C}$, $Q \times f = 12,500$) [15, 36-38] and KMO ($\epsilon_r = 6.4$, $\text{TCF} = -70\text{ ppm}/^{\circ}\text{C}$, $Q \times f = 26,500$) [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 Bi₂O₃ (99.9%, Acros Organics) and MoO₃ (>99%, Acros Organics) were weighed with a Bi₂O₃: MoO₃ 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 α radiation), Renishaw inVia Raman microscope Raman spectroscopy and an FEI Inspect F-50 scanning electron microscopy (SEM). The TE₀₁₈ 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 TE₀₁₈ resonant frequencies at temperatures, T and T₀, respectively.

3. Results and discussion

The relative density (ρ_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 (ρ_r), and microwave dielectric properties of BMO-KMO ceramics.

Composition	ST (°C)	ρ_r (%)	ϵ_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 $P121/n1$ (ICSD: 201742) and $C12/m1$ (ICSD: 16154) symmetry, respectively.[15, 33, 34, 36-38] B-site Mo^{6+} cations are coordinated by four O-anions, leading to tightly bound MoO_4 tetrahedra. The A-site Bi^{3+} or 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 $a = 11.9515$ Å, $b = 10.8007$ Å, $c = 11.8814$ Å for BMO and $a = 12.672$ Å, $b = 6.030$ Å, $c = 7.066$ Å 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 cm^{-1} , which were assigned to bending (260 ~ 380 cm^{-1}) and stretching (739 ~ 888 cm^{-1}) modes of MoO_4 tetrahedra and the conversion of Mo/Bi atoms (< 260 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 100~160 cm^{-1} correspond to a combination of the translations and vibrations of MoO_4 tetrahedra and translations of K ions. The 310~370 cm^{-1} bands are related to bending modes of MoO_4 tetrahedra. The 820~890 cm^{-1} bands are related to stretching modes of 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. ϵ_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 ϵ_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 ε_1 is the ε_r of phase 1, ε_2 is the ε_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. ε_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 TCF_1 and 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 $20\text{ mm} \times 20\text{ mm} \times 2\text{ mm}$ to $\sim 40\text{ mm} \times 40\text{ mm} \times 7\text{ mm}$ 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 $>1200\text{ }^{\circ}\text{C}$ 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 ($>1200\text{ }^{\circ}\text{C}$) but cold sintering densifies powders at less than the melting point ($<200\text{ }^{\circ}\text{C}$) 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 $30\text{ mm} \times 30\text{ mm} \times 7\text{ mm}$ were directly cold-sintered onto an $85\text{ mm} \times 75\text{ mm} \times 1.6\text{ mm}$ 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 $18.5\text{ mm} \times 18.5\text{ mm}$ 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 $\sim 45\text{ }\mu\text{m}$ 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, ϵ_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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References

- [1] I.M. Reaney, D. Iddles, Microwave dielectric ceramics for resonators and filters in mobile phone networks, *J Am Ceram Soc* 89(7) (2006) 2063-2072.
- [2] T. Ibn-Mohammed, C.A. Randall, K. Mustapha, J. Guo, J. Walker, S. Berbano, S. Koh, D. Wang, D. Sinclair, I. Reaney, Decarbonising ceramic manufacturing: A techno-economic analysis of energy efficient sintering technologies in the functional materials sector, *J Eur Ceram Soc* 39(16) (2019) 5213-5235.
- [3] Z. Song, K. Song, B. Liu, P. Zheng, H. Barzegar Bafrooei, W. Su, H. Lin, F. Shi, D. Wang, I. Reaney, Temperature-dependent dielectric and Raman spectra and microwave dielectric properties of gehlenite-type $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ceramics, *International Journal of Applied Ceramic Technology* 17(2) (2020) 771-777.
- [4] Q. Lin, K. Song, B. Liu, H.B. Bafrooei, D. Zhou, W. Su, F. Shi, D. Wang, H. Lin, I.M. Reaney, Vibrational spectroscopy and microwave dielectric properties of $\text{AY}_2\text{Si}_3\text{O}_{10}$ (A= Sr, Ba) ceramics for 5G applications, *Ceram Int* 46(1) (2020) 1171-1177.
- [5] D. Zhou, D. Guo, W.B. Li, L.X. Pang, X. Yao, D.W. Wang, I.M. Reaney, Novel temperature stable high- ϵ_r microwave dielectrics in the $\text{Bi}_2\text{O}_3\text{--TiO}_2\text{--V}_2\text{O}_5$ system, *J Mater Chem C* 4(23) (2016) 5357-5362.
- [6] H.H. Guo, D. Zhou, W.F. Liu, L.X. Pang, D.W. Wang, J.Z. Su, Z.M. Qi, Microwave dielectric properties of temperature-stable zircon-type $(\text{Bi,Ce})\text{VO}_4$ solid solution ceramics, *J Am Ceram Soc* 103(1) (2020) 423-431.
- [7] H.H. Guo, D. Zhou, L.X. Pang, Z.M. Qi, Microwave dielectric properties of low firing temperature stable scheelite structured $(\text{Ca,Bi})(\text{Mo,V})\text{O}_4$ solid solution ceramics for LTCC applications, *J Eur Ceram Soc* 39(7) (2019) 2365-2373.

- [8] D. Zhou, L.X. Pang, D.W. Wang, I.M. Reaney, BiVO₄ based high k microwave dielectric materials: a review, *J Mater Chem C* 6(35) (2018) 9290-9313.
- [9] D. Zhou, L.X. Pang, D.W. Wang, Z.M. Qi, I.M. Reaney, High quality factor, ultralow sintering temperature Li₆B₄O₉ microwave dielectric ceramics with ultralow density for antenna substrates, *Acs Sustain Chem Eng* 6(8) (2018) 11138-11143.
- [10] L.X. Pang, D. Zhou, D.W. Wang, J.X. Zhao, W.G. Liu, Z.X. Yue, I.M. Reaney, Temperature stable K_{0.5}(Nd_{1-x}Bi_x)_{0.5}MoO₄ microwave dielectrics ceramics with ultra-low sintering temperature, *J Am Ceram Soc* 101(5) (2018) 1806-1810.
- [11] D. Zhou, L.X. Pang, D.W. Wang, H.H. Guo, F. Yang, Z.M. Qi, C. Li, B.B. Jin, I.M. Reaney, Crystal structure, impedance and broadband dielectric spectra of ordered scheelite-structured Bi(Sc_{1/3}Mo_{2/3})O₄ ceramic, *J Eur Ceram Soc* 38(4) (2018) 1556-1561.
- [12] D. Zhou, L.X. Pang, D.W. Wang, C. Li, B.B. Jin, I.M. Reaney, High permittivity and low loss microwave dielectrics suitable for 5G resonators and low temperature co-fired ceramic architecture, *J Mater Chem C* 5(38) (2017) 10094-10098.
- [13] D. Zhou, J. Li, L.-X. Pang, D.-W. Wang, I.M. Reaney, Novel water insoluble (Na_xAg_{2-x})MoO₄ (0 ≤ x ≤ 2) microwave dielectric ceramics with spinel structure sintered at 410 degrees, *J Mater Chem C* 5(24) (2017) 6086-6091.
- [14] D. Zhou, J. Li, L.-X. Pang, G.-H. Chen, Z.-M. Qi, D.-W. Wang, I.M. Reaney, Crystal structure, infrared spectra, and microwave dielectric properties of temperature-stable zircon-type (Y,Bi)VO₄ solid-solution ceramics, *Acs Omega* 1(5) (2016) 963-970.
- [15] R. Gheisari, H. Chamberlain, G. Chi-Tangyie, S. Zhang, A. Goulas, C.-K. Lee, T. Whittaker, D. Wang, A. Ketharam, A. Ghosh, Multi-material additive manufacturing of low sintering temperature Bi₂Mo₂O₉ ceramics with Ag floating electrodes by selective laser burnout, *Virtual and Physical Prototyping* 15(2) (2020) 133-147.

- [16] H. Kahari, M. Teirikangas, J. Juuti, H. Jantunen, Dielectric Properties of Lithium Molybdate Ceramic Fabricated at Room Temperature, *J Am Ceram Soc* 97(11) (2014) 3378-3379.
- [17] H. Kahari, M. Teirikangas, J. Juuti, H. Jantunen, Room-temperature fabrication of microwave dielectric $\text{Li}_2\text{MoO}_4\text{-TiO}_2$ composite ceramics, *Ceram Int* 42(9) (2016) 11442-11446.
- [18] M. Vaataja, H. Kahari, J. Juuti, H. Jantunen, Li_2MoO_4 -based composite ceramics fabricated from temperature- and atmosphere-sensitive MnZn ferrite at room temperature, *J Am Ceram Soc* 100(8) (2017) 3626-3635.
- [19] M. Vaataja, H. Kahari, K. Ohenoja, M. Sobocinski, J. Juuti, H. Jantunen, 3D printed dielectric ceramic without a sintering stage, *Sci Rep-Uk* 8 (2018).
- [20] J. Guo, H.Z. Guo, A.L. Baker, M.T. Lanagan, E.R. Kupp, G.L. Messing, C.A. Randall, Cold Sintering: A Paradigm Shift for Processing and Integration of Ceramics, *Angew Chem Int Edit* 55(38) (2016) 11457-11461.
- [21] J. Guo, S.S. Berbano, H.Z. Guo, A.L. Baker, M.T. Lanagan, C.A. Randall, Cold Sintering Process of Composites: Bridging the Processing Temperature Gap of Ceramic and Polymer Materials, *Adv Funct Mater* 26(39) (2016) 7115-7121.
- [22] A. Baker, H.Z. Guo, J. Guo, C. Randall, Utilizing the Cold Sintering Process for Flexible-Printable Electroceramic Device Fabrication, *J Am Ceram Soc* 99(10) (2016) 3202-3204.
- [23] J. Guo, A.L. Baker, H.Z. Guo, M. Lanagan, C.A. Randall, Cold sintering process: A new era for ceramic packaging and microwave device development, *J Am Ceram Soc* 100(2) (2017) 669-677.
- [24] J.P. Maria, X.Y. Kang, R.D. Floyd, E.C. Dickey, H.Z. Guo, J. Guo, A. Baker, S. Funihashi, C.A. Randall, Cold sintering: Current status and prospects, *J Mater Res* 32(17) (2017) 3205-3218.
- [25] J. Guo, X.T. Zhao, T.H. De Beauvoir, J.H. Seo, S.S. Berbano, A.L. Baker, C. Azina, C.A. Randall, Recent Progress in Applications of the Cold Sintering Process for Ceramic-Polymer Composites, *Adv Funct Mater* 28(39) (2018).

- [26] I.J. Induja, M.T. Sebastian, Microwave dielectric properties of mineral sillimanite obtained by conventional and cold sintering process, *J Eur Ceram Soc* 37(5) (2017) 2143-2147.
- [27] W.B. Hong, L. Li, M. Cao, X.M. Chen, Plastic deformation and effects of water in room-temperature cold sintering of NaCl microwave dielectric ceramics, *J Am Ceram Soc* 101(9) (2018) 4038-4043.
- [28] Y. Liu, P. Liu, C.X. Hu, Low-temperature preparation and microwave dielectric properties of cold sintered $\text{Li}_2\text{Mg}_3\text{TiO}_6$ nanocrystalline ceramics, *Ceram Int* 44(17) (2018) 21047-21052.
- [29] S.S. Faouri, A. Mostaed, J.S. Dean, D.W. Wang, D.C. Sinclair, S.Y. Zhang, W.G. Whittow, Y. Vardaxoglou, I.M. Reaney, High quality factor cold sintered $\text{Li}_2\text{MoO}_4\text{-BaFe}_{12}\text{O}_{19}$ composites for microwave applications, *Acta Mater* 166 (2019) 202-207.
- [30] D. Zhou, L.X. Pang, D.W. Wang, I.M. Reaney, Novel water-assisting low firing MoO_3 microwave dielectric ceramics, *J Eur Ceram Soc* 39(7) (2019) 2374-2378.
- [31] Y. Ji, K. Song, X. Luo, B. Liu, H. Barzegar Bafrooei, D. Wang, Microwave dielectric properties of $(1-x) \text{Li}_2\text{MoO}_4\text{-xMg}_2\text{SiO}_4$ composite ceramics fabricated by cold sintering process, *Frontiers in Materials* 6 (2019) 256.
- [32] D.W. Wang, D. Zhou, S.Y. Zhang, Y. Vardaxoglou, W.G. Whittow, D. Cadman, I.M. Reaney, Cold-Sintered Temperature Stable $\text{Na}_{0.5}\text{Bi}_{0.5}\text{MoO}_4\text{-Li}_2\text{MoO}_4$ Microwave Composite Ceramics, *Acs Sustain Chem Eng* 6(2) (2018) 2438-2444.
- [33] D.W. Wang, S.Y. Zhang, D. Zhou, K.X. Song, A. Feteira, Y. Vardaxoglou, W. Whittow, D. Cadman, I.M. Reaney, Temperature Stable Cold Sintered $(\text{Bi}_{0.95}\text{Li}_{0.05})(\text{V}_{0.9}\text{Mo}_{0.1})\text{O}_4\text{-Na}_2\text{Mo}_2\text{O}_7$ Microwave Dielectric Composites, *Materials* 12(9) (2019).
- [34] D. Wang, S. Zhang, G. Wang, Y. Vardaxoglou, W. Whittow, D. Cadman, D. Zhou, K. Song, I.M. Reaney, Cold sintered $\text{CaTiO}_3\text{-K}_2\text{MoO}_4$ microwave dielectric ceramics for integrated microstrip patch antennas, *Applied Materials Today* 18 (2020) 100519.
- [35] D.W. Wang, D. Zhou, K.X. Song, A. Feteira, C.A. Randall, I.M. Reaney, Cold-Sintered C0G Multilayer Ceramic Capacitors, *Adv Electron Mater* 5(7) (2019).

- [36] D. Zhou, H. Wang, L.X. Pang, C.A. Randall, X. Yao, Bi₂O₃-MoO₃ Binary System: An Alternative Ultralow Sintering Temperature Microwave Dielectric, *J Am Ceram Soc* 92(10) (2009) 2242-2246.
- [37] D. Zhou, H. Wang, X. Yao, L.X. Pang, Microwave Dielectric Properties of Low Temperature Firing Bi₂Mo₂O₉ Ceramic, *J Am Ceram Soc* 91(10) (2008) 3419-3422.
- [38] D. Zhou, C.A. Randall, A. Baker, H. Wang, L.X. Pang, X. Yao, Dielectric Properties of an Ultra-Low-Temperature Cofiring Bi₂Mo₂O₉ Multilayer, *J Am Ceram Soc* 93(5) (2010) 1443-1446.
- [39] F.D. Hardcastle, I.E. Wachs, Molecular-Structure of Molybdenum Oxide in Bismuth Molybdates by Raman-Spectroscopy, *J Phys Chem-Us* 95(26) (1991) 10763-10772.
- [40] K. Seevakan, A. Manikandan, P. Devendran, Y. Slimani, A. Baykal, T. Alagesan, Structural, magnetic and electrochemical characterizations of Bi₂Mo₂O₉ nanoparticle for supercapacitor application, *J Magn Magn Mater* 486 (2019).
- [41] W. Paraguassu, G.D. Saraiva, S. Guerini, P.T.C. Freire, B.T.O. Abagaro, J. Mendes, Pressure-induced phase transition on K₂MoO₄: A Raman scattering study and ab initio calculations, *J Solid State Chem* 196 (2012) 197-202.
- [42] G.D. Saraiva, W. Paraguassu, P.T.C. Freire, M. Maczka, J. Mendes, Temperature-dependent Raman scattering study of K₂MoO₄, *Vib Spectrosc* 58 (2012) 87-94.