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# Low temperature co-fired ceramics with ultra-low sintering temperature: A review

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ABSTRACT

The recent rapid advances in wireless telecommunication, Internet of Things, the Tactile Internet (5th generation wireless systems), the Industrial Internet, electronic warfare, satellite broadcasting, and intelligent transport systems demand low loss dielectric materials with ultra-low sintering temperatures with modern component fabrication techniques. Properties of microwave ceramics depend on several parameters including their composition, the purity of starting materials, processing conditions, and their ultimate densification/porosity. The preparation, characterization and properties of important materials families such as glass ceramics and molybdates, tellurates, tungstates and vanadates, in combination with Bi, K, Na, Ag, Li, Ba, Ca, etc. with ultra-low sintering temperatures are discussed. In this review the data for all reported low-loss microwave dielectric ceramic materials with ultra-low sintering temperatures are collected and tabulated. The table of these materials gives the relative permittivity, quality factor ($\tan\delta$), temperature variation of the resonant frequency, crystal structure, sintering temperature, measurement frequency and references. The data arranged in the order of increasing relative permittivity will be very useful for scientists, industrialists, engineers and students working on current and emerging applications of microelectronics.



## 1. Introduction

The demand for different types of ceramics with varying microwave dielectric properties is rapidly increasing for applications in the ever growing wireless communication and broadcasting industry. An interconnected wireless world with several multifunctional sensors and processing devices has come to a reality. This has become possible with the help of smart phones, tablets, cameras, RF identification tags, wearable devices and sensors which are all connected through several public and private wireless equipment. The wireless technologies enabling the Internet of Things (IoT) and Machine-to-Machine (M2M) devices have customized requirements and performance criteria for each application. The multilayer cofired ceramic technologies are used to fabricate several devices such as band pass filters, oscillators, wave guides, and antennas for miniaturization of microwave components in wireless communication. The important characteristics required for practical applications are suitable relative permittivity (high for miniaturization and low for fast signal transmission), low dielectric loss, temperature stable dielectric properties, matched CTE with other materials in integrations, low sintering temperature below that of the electrode materials, high thermal conductivity, chemical compatibility with electrode material, etc. The toxicity and cost effectiveness of the materials are also very important. A large number of low loss ceramic dielectric materials are reported in the literature [1–3]. However, most of these materials have high sintering temperatures, which preclude their usage and integration with other materials such as low melting electrode, semiconductors such as silicon or GaAs and polymer based substrates. The high processing temperature also leads to large energy consumption, evaporation of volatile components and reactions with other materials. For practical applications, the dielectric material should be chemically compatible with the electrode material. The Low Temperature Cofired Ceramic (LTCC) technology is reasonably well developed [2]. In LTCC the green dielectric tape with passive components is cofired with the common electrode silver at temperatures less than the melting point of silver (961 °C). Slightly higher cofiring temperatures are possible with copper or gold electrodes.

Currently intensive search is going on to find materials with ultra-low firing temperatures less than 700 °C and the number of papers published on ULTCC is rapidly increasing. Most of the high quality factor (Q) dielectric materials have high sintering

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temperatures and can be lowered by adding low melting glasses but it often degrades the microwave dielectric properties. The densification in this case is achieved by liquid phase sintering. Addition of low melting compounds $TeO_2$, $Bi_2O_3$, $B_2O_3$, $Li_2O$, $V_2O_5$, $MoO_3$, etc. can lower the sintering temperature of parent materials. However, large amount of these low melting sintering aids also degrade the microwave dielectric properties. In addition there are materials with inherently ultra-low sintering temperatures. Valant and Suvorov were the first to report [4] the microwave dielectric properties of ULTCC materials. They reported that $Bi_{12}PbO_{19}$ sillenite which has a body centered cubic structure can be sintered at 680 °C. This material has $\varepsilon_r$ of 38.6, a low Qf of 2900 GHz and $\tau_f$ of −84 ppm/°C. Pure $Bi_2O_3$ can be sintered at 680 °C and show a relative permittivity of 33.5, Qf of 18,700 GHz and a high negative $\tau_f$ of 235 [5]. The reported materials with ultra-low sintering temperature are found to be mostly based on tellurates, molybdates, vanadates, and tungstates in combination with Bi, K, Na, Ag, Li, Ba, etc. and glasses or glass ceramic composites. The application of these materials is limited because many of these materials are chemically incompatible with the common electrode silver. Recently Sebastian and Jantunen made a review on LTCC for materials with sintering temperature up to 1000 °C [2]. The purpose of the present report is to review the current status of materials for ULTCC technology with sintering temperature less than 700 °C. The development of ULTCC materials with a sintering temperature less than 700 °C are still in its infant stage and currently only a handful of materials with good properties are available for practical applications in this rapidly and demanding sector of microelectronics.

## 2. Ultra-low temperature sinterable materials

### 2.1. Glasses and glass–ceramics

There are excellent microwave dielectric materials with very useful dielectric properties [3]. However, their sintering temperatures are in general relatively high. Recently extensive researches have been carried out to find materials cofireable with silver or aluminum electrodes for miniaturization of microwave devices. Reduction of the sintering temperature of the ceramic material to a level such that it can be cofired with silver is essential. Generally glass materials with low softening temperature is mixed with ceramics to lower the sintering temperature. However, the network formers in the glasses in general may absorb microwave energy considerably at high frequencies that increase the loss tangent of the composite. However, there are several glasses with relatively low loss factor in the microwave frequency regime. In this review only the glasses with low softening or sintering temperatures (less than 700 °C) are discussed. The glass based ULTCC materials are often multiphase, in which properties not only depend on the properties of the individual phases but also on the microstructure, morphology, continuity, etc. of each phase. Also for ULTCC fabrication good densification and crystallinality are required for good dielectric and mechanical properties. The effectiveness of glass additives as sintering aids on microwave ceramics depends on several factors such as sintering temperature, viscosity, solubility, wetting behavior etc. Glass–ceramic and glass + ceramic routes are commonly used to develop glass based LTCC or ULTCC materials [6,7]. Glass–ceramics are polycrystalline materials that are initially a glassy system and devitrifies almost completely during the sintering process. The end properties of glass–ceramic system depend on the degree of crystallization, which can be controlled by the addition of a small amount of suitable nucleating agent. In the glass + ceramic approach, a low softening point glass and a crystalline ceramic are initially mixed. The densification is achieved through liquid phase sintering. The liquid glass penetrates the 3D mesh structure of the ceramic and wets the ceramic particles to effect the densification of the ceramic body. In general, the commercially available LTCC systems are either glass–ceramic or glass + ceramic.

Chen et al. [8] reported the microwave dielectric properties of $MO–B_2O_3–SiO_2$ (M = Mg, Ba or Sr) glasses. These glasses have a softening temperature ($T_s$) in the range 560–613 °C reaching the lowest temperature with Ba. The Ba based glass has the highest relative permittivity ($\varepsilon_r$) of 7.6 with a quality factor of (Qf) of about 4100 GHz. $CaO–B_2O_3–SiO_2$ glass ceramic system is extensively studied for LTCC applications [9–15] and is commercially produced by Ferro and some other companies. These glasses have a softening temperature in the range 650–710 °C depending on the composition and sintering temperature of the glass–ceramic in the range 700–1000 °C. The glasses crystallize partially on sintering and lower the dielectric loss factor. The glass–ceramics have a relative permittivity in the range 4–8 and losses less than 0.005 in the microwave frequency range. Wu and Huang [16] made a detailed investigation on the microwave dielectric properties of barium, zinc and lead based borosilicate glasses for different compositions. Fig. 1a and b shows the variation glass transition temperature ($T_g$) and relative permittivity of ZBS ($ZnO–B_2O_3–SiO_2$) and BBS ($BaO–B_2O_3–SiO_2$) as a function of $B_2O_3$ content, respectively. Fig. 2a and b shows the variation of $T_g$ and relative permittivity of PBS ($PbO–B_2O_3–SiO_2$) glass with PbO content. The $\varepsilon_r$, Qf and $\tau_f$ are given in a Table as supplementary file. In Zn and Ba based glasses (Fig. 1a), an increase in $B_2O_3$ content lowered the glass transition temperature ($T_g$) whereas an increase in Pb content and a decrease in $B_2O_3$ content lowered the $T_g$ for the Pb based glasses. The Zn and Ba based glasses have a $T_g$ in the range 550–720 °C depending on the compositions whereas for Pb based glass it was in the range 312–500 °C. The Qf and $\tau_f$ decrease with PbO content in the case of Pb based glasses. It is found [16] that the microwave dielectric properties $\varepsilon_r$ and Qf mainly depend on the network modifiers in the glasses. The Qf of these glasses varies in the range 500–3400 GHz.

Yu and co-workers [17–20] reported that $3ZnO–2B_2O_3$ glass ceramic sintered at 650 °C for 30 min has excellent dielectric properties. The glass ceramic composites showed $\varepsilon_r$ of 7.5 and $\tan\delta$ of $6 \times 10^{-4}$ at 10 MHz. Addition of 15 wt% $SiO_2$ and sintered at 650 °C for 30 min lowered $\varepsilon_r$ to 6.1 with $\tan\delta = 1.3 \times 10^{-3}$ at 1 MHz. Yu et al. [19] also prepared $SiO_2$ filled zinc borate glass composite ULTCC tapes. The ULTCC laminated 5-layer tape sintered at 650 °C showed $\varepsilon_r$ of 6.4 with $\tan\delta$ of 0.001 at 1 MHz. Fig. 3a shows the SEM cross-section micrograph of $3ZnO–2B_2O_3$ + 15 wt% $SiO_2$ laminated ceramic tapes cofired with silver electrode at 650 °C for 30 min. The $ZnO–B_2O_3$ based glass ceramics do not react with silver and are suitable candidates for ULTCC applications. Fig. 3b shows the variation of dielectric properties and bulk densities of silica filled zinc borate glass sintered at different temperatures for 30 min. The composite shows the best dielectric properties and density when sintered at 650 °C for 30 min.

Rajesh et al. [21] prepared glass + alumina composites with ultra-low sintering temperatures cofireable with silver electrodes. They used the commercial glasses G018-249 and G018-250 with glass transition temperatures $T_g$ of 365 and 380 °C respectively. The G018-249 glass frit is alkali free and contains large amount of $Bi_2O_3$ and ZnO whereas the G018-250 is a solder glass containing $Li_2O$ and $Bi_2O_3$. The alumina filler used was about 50 wt% and well densified on sintering at 650 °C. The composites did not react with silver electrode material on sintering at 650 °C. The G018-249 and G018-250 composites with alumina sintered at 650 °C showed a relative permittivity of 9.5 and 8.85, loss tangents 0.0068 and 0.0087 at 1 MHz and bulk densities of 3.62 and 3.99 g/cm$^3$ respectively. Fig. 4 shows the variation of the relative permittivity and loss tangents as a

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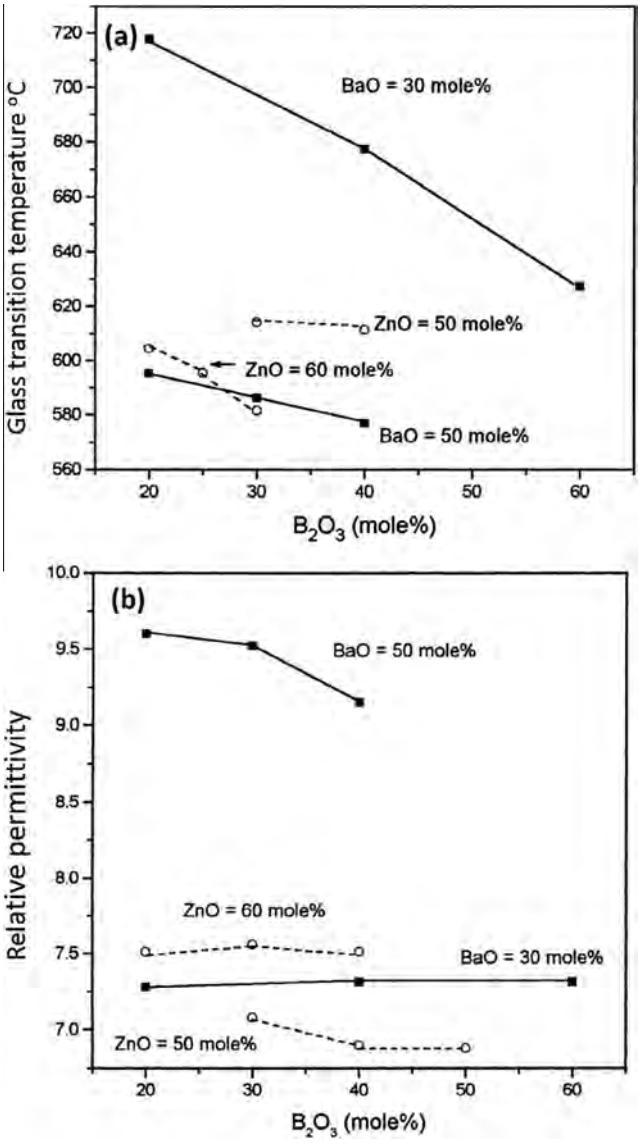


**Fig. 1.** Variation (a) of glass transition temperature as a function of $B_2O_3$ content (O) $ZnO–B_2O_3–SiO_2$, □ $BaO–B_2O_3–SiO_2$ glasses (b) relative permittivity as a function of $B_2O_3$ content (O) $ZnO–B_2O_3–SiO_2$, □ $BaO–B_2O_3–SiO_2$ glasses (after Wu and Huang [16]. Reproduced with permission from Elsevier).

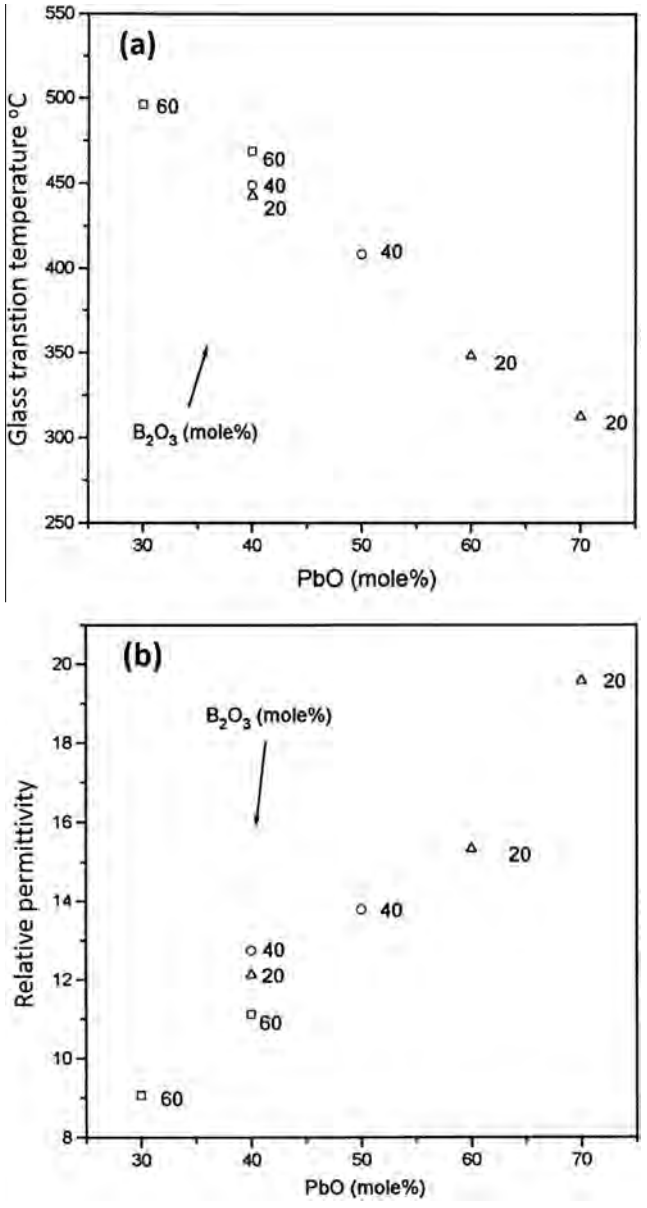


**Fig. 2.** Variation of (a) glass transition temperature (b) relative permittivity of $PbO–B_2O_3–SiO_2$ glasses as a function of PbO content (after Wu and Huang [16]. Reproduced with permission from Elsevier).

function of temperature in the range 0–80 °C and measured at 1 MHz. The temperature coefficient of relative permittivities were 316 and 426 ppm/°C for the two samples, respectively.

More recently Chen et al. [22,23] reported that addition of a large amount of BBSZ ($27B_2O_3–35Bi_2O_3–6SiO_2–32ZnO$ in mol%) could effectively lower the sintering temperature of $Al_2O_3$ and $BaTiO_3$ ceramics to a level of about 450 °C with relatively low dielectric loss tangent. Fig. 5 shows the shrinkage behavior of BBSZ–$BaTiO_3$ composite using a dilatometer. The shrinkage of the composites started at about 382 °C, which is close to the glass transition temperature of the BBSZ glass. The BBSZ glass has a relative permittivity of about 21 [24] and hence the relative permittivity of alumina composite is expected to increase and that of $BaTiO_3$ based to decrease. The dielectric properties and sintering temperatures of the different composites are given in the supplementary file which are arranged in the order of increasing relative permittivity. The $BaTiO_3$ composite containing 50 wt% BBSZ glass sintered at 450 °C has $\varepsilon_r$ = of 136 with a tan $\delta$ of 0.020 at 100 MHz. The $\varepsilon_r$ and tan $\delta$ decrease to 63 and 0.011 respectively at 100 MHz on increasing the BBSZ content to 90 wt%. X-ray diffraction study of the BBSZ–$Al_2O_3$ and BBSZ–$BaTiO_3$ composites sintered at 450 °C revealed the presence of $Bi_{24}Si_2O_{40}$ secondary phase. Fig. 6 shows the SEM micrograph of the BBSZ composite containing $Al_2O_3$ fillers showing the presence of different phases. The dielectric properties of the composites are influenced by the amount of co-existing ceramic filler, BBSZ glass and the secondary phase $Bi_{24}Si_2O_{40}$. The relative permittivity of the composite can be tailored by the amount of ceramic fillers keeping the sintering temperature close to 450 °C. The $\varepsilon_r$ of BBSZ-alumina increases above that of BBSZ and is attributed to the presence of secondary phase $Bi_{24}Si_2O_{40}$, which has a high $\varepsilon_r$ of 37.6 with Qf of 8100 GHz [4]. However, Kim et al. observed $ZnAl_2O_4$ secondary phase instead of $Bi_{24}Si_2O_{40}$ in BBSZN with a slightly different composition and containing a small amount of $Na_2O$ ($22.7Bi_2O_3–23.3B_2O_3–13.5SiO_2–37.9ZnO–2.6Na_2O$ mol%) [25]. The BBSZN has a low $\varepsilon_r$ of 15.3, of 1500 GHz and $\tau_f$ −40 ppm/°C. The BBSZN with 50 vol% $Al_2O_3$ sintered at 700 °C showed $\varepsilon_r$ of about 9.5, Qf = 3200 GHz and $\tau_f$ = 119 ppm/°C [25].

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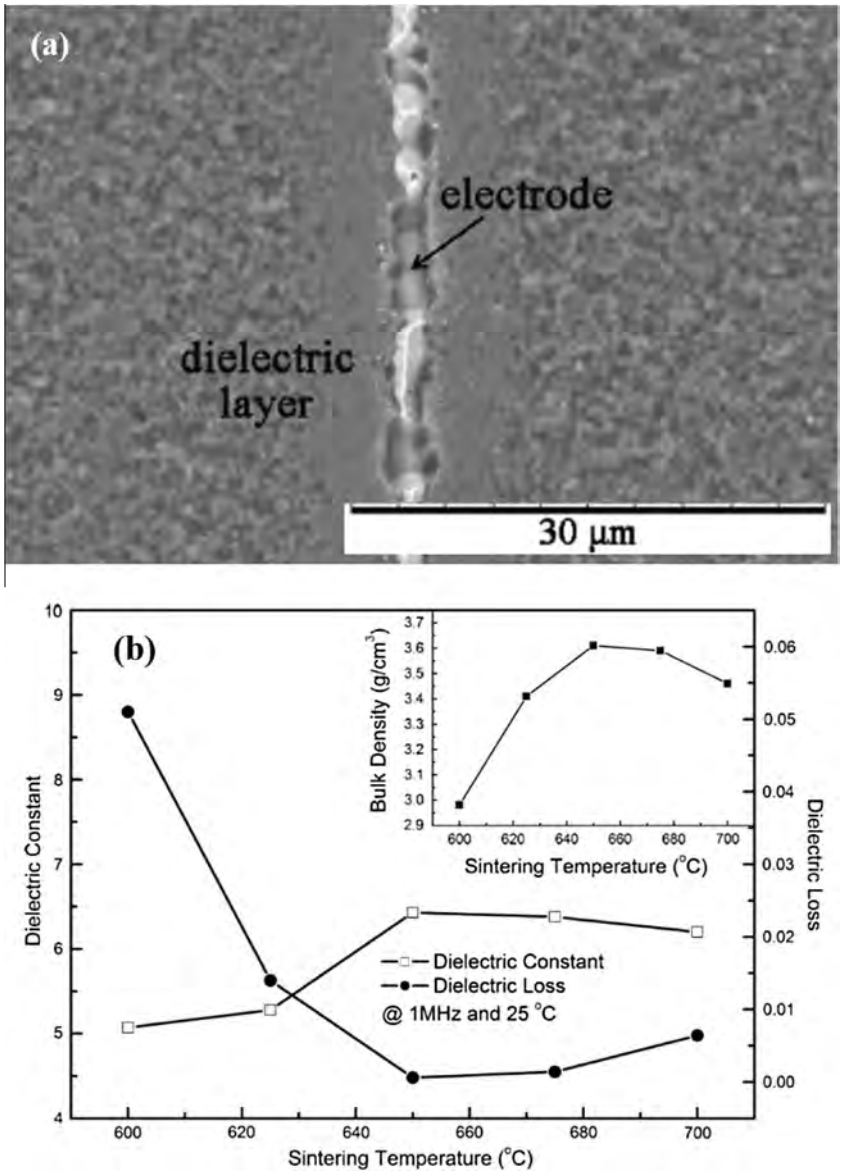


**Fig. 3.** (a) Scanning electronic micrograph of the cross-section of $3ZnO–2B_2O_3–15$ wt% $SiO_2$ ULTCC laminated tape co-fired with Ag at 650 °C for 30 min. (b) Dielectric properties of $3ZnO–2B_2O_3–SiO_2$ bulk ceramics sintered at different temperatures for 30 min. The inset shows the variation of bulk density (after Yu et al. [19]. Reproduced with permission from Springer).

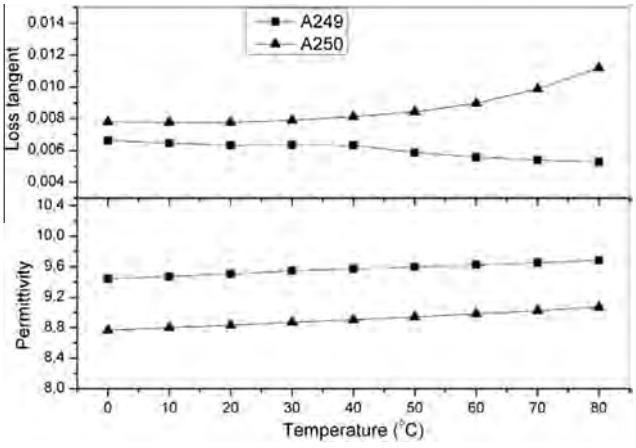


**Fig. 4.** Variation of dielectric properties of G018-249 and G018-250 composites with alumina as a function of temperature at 1 MHz (after Rajesh et al. [21]).

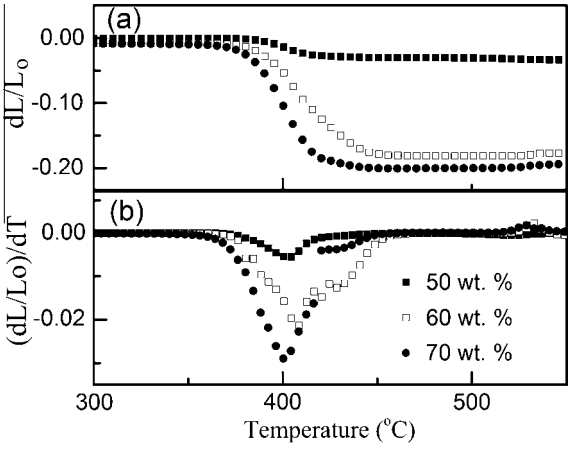


**Fig. 5.** (a) Shrinkage behavior of BBSZ–$BaTiO_3$ composites and (b) their derivation (after Chen et al. [22]).

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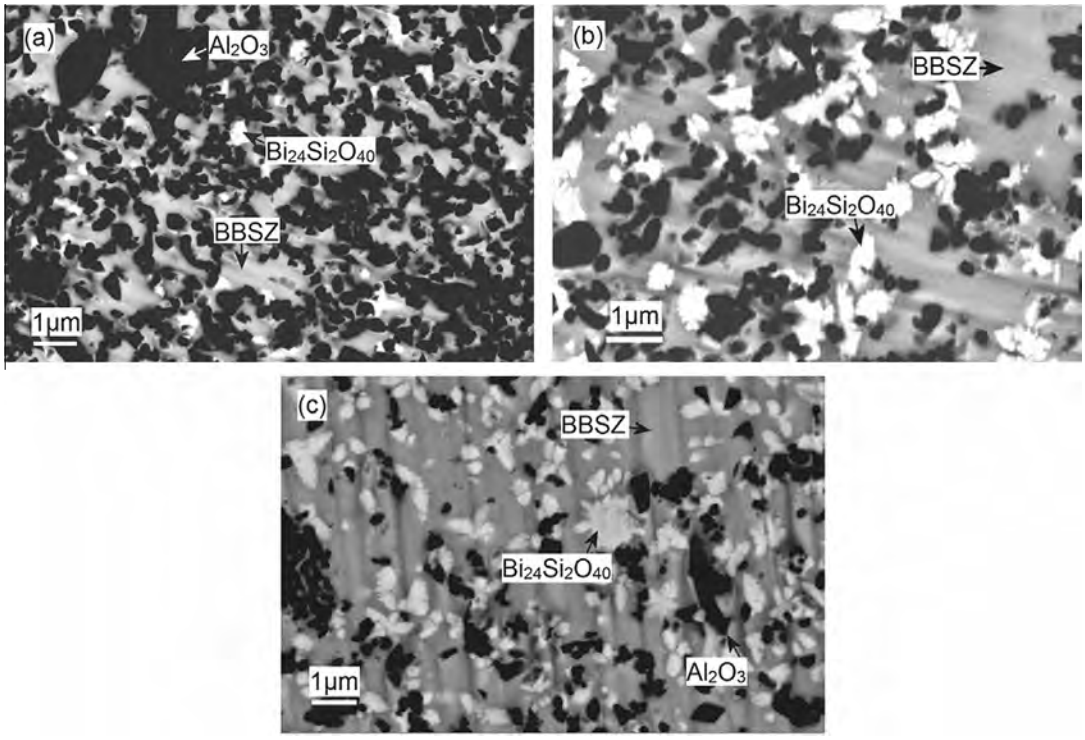


**Fig. 6.** Backscattered SEM image of the BBSZ–$Al_2O_3$ composite (a) 30 vol% (b) 20 vol% $Al_2O_3$ content sintered at 450 °C (after Chen et al. [23]).

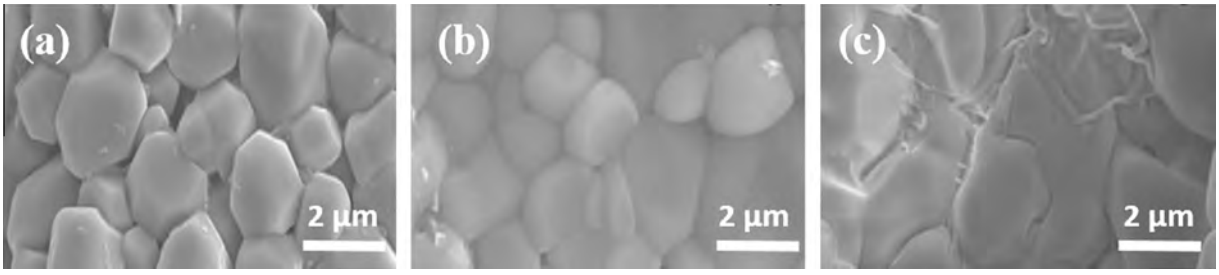


**Fig. 7.** SEM picture of $Ba_3V_4O_{13}$ ceramics sintered at (a) 580 °C, (b) 600 °C, and (c) 620 °C for 1 h (after Kalathil et al. [39]. Reproduced with permission from John Wiley & Sons).

The glass based ceramic materials are potential candidates for packaging applications using silver or aluminum based electrodes.

### 2.2. Vanadates

Valant et al. in 2000 reported [26] that $BiVO_4$ ceramic has good microwave dielectric properties with a low sintering temperatures. Since then several vanadates compounds such as $Mg_3(VO_4)_2$, $R_2V_2O_7$ (R = Ba, Sr, Ca, Mg, and Zn), $Ba_3MV_4O_{15}$ (M = Ti, and Zr), $NaCa_2Mg_2V_3O_{12}$, $LiMg_4V_3O_{12}$, $Ca_5Zn_4(VO_4)_6$ have been investigated for LTCC applications [1,25–35]. However, these materials have sintering temperature above 700 °C, which is higher than what is needed for ULTCC. More recently, a few new vanadium based compounds such as $LiMgVO_4$, $LiZnVO_4$, $BaV_2O_6$, $Ba_3V_4O_{13}$ and $Na_2BiMg_2V_3O_{12}$ have been reported [26,33–42] for ultra-low temperature cofired applications with sintering temperatures less than 700 °C. The orthorhombic $BaV_2O_6$ can be well sintered at 550 °C for 1 h with excellent microwave dielectric properties [41]. The XRD and EDS analysis revealed the chemical compatibility of $BaV_2O_6$ with Al electrode material. This material with a relative permittivity $\varepsilon_r$ of 11.2, high quality factor of 42,800 GHz and $\tau_f$ of 28 ppm/°C is a potential candidate for ULTCC application utilizing Al electrodes. Another similar compound with very high quality factor is monoclinic $CaV_2O_6$ with a $\varepsilon_r$ of 10.2, Qf of 123,000 GHz and $\tau_f$ of −60 ppm/°C when sintered at 675 °C [42].

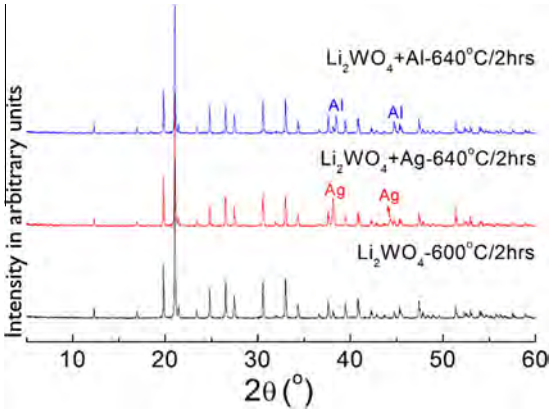


**Fig. 8.** X-ray diffraction patterns of $Li_2WO_4$ ceramics sintered at 600 °C and cofired ceramics with 20 wt% Ag and 20 wt% Al at 640 °C for 2 h (after Zhou et al. [43]).

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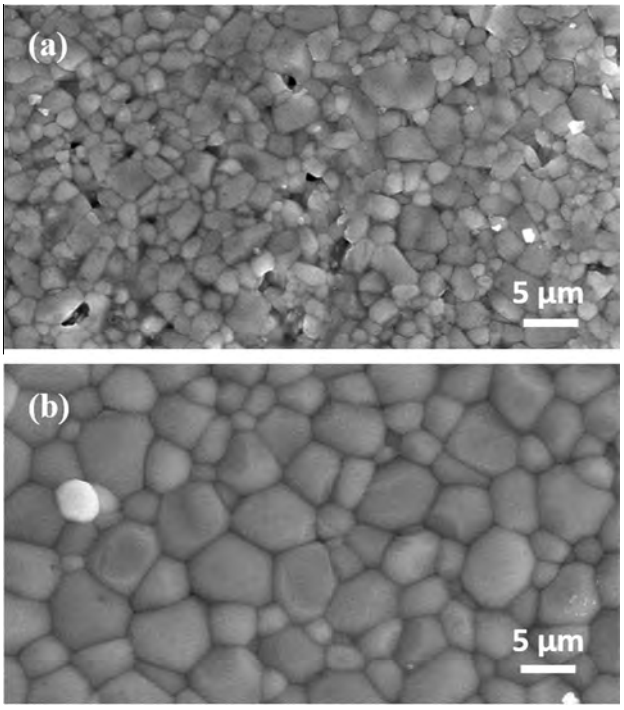


**Fig. 9.** SEM micrograph of (a) $Pb_2WO_5$ sintered at 530 °C (b) $PbWO_4$ sintered at 620 °C (after Xie et al. [48]. Reproduced with permission from John Wiley & Sons).

The $Ba_3V_4O_{13}$ has a monoclinic crystal structure with space group I2/a and the ceramic sintered at 600 °C for 1 h shows excellent microwave dielectric properties. It has $\varepsilon_r$ of 9.6, Qf of 56,100 GHz and $\tau_f$ of −42 ppm/°C and is cofireable with Al [39]. Fig. 7 shows the microstructure of the $Ba_3V_4O_{13}$ ceramic sintered at 600 °C for 1 h revealing densely packed grains. The $Na_2BiMg_2V_3O_{13}$ ceramic has a cubic garnet structure and the ceramic showed the best density when sintered at 660 °C and has $\varepsilon_r$ of 23.2 [36]. However, it has a relatively low Qf of 3700 GHz with $\tau_f$ of 8 ppm/°C and the compatibility with Ag or Al electrode has not been reported. The orthorhombic $LiMgVO_4$ could be well sintered at 675 °C and shows a good relative permittivity (9.5) and a high quality factor 34,800 GHz. However, it reacts with Ag and has a poor $\tau_f$ value of −146 ppm/°C [37,38]. The high $\tau_f$ value can be tailored by adding a small amount of $TiO_2$ but it increases the sintering temperatures to above 700 °C [37]. The $LiZnVO_4$ is rhombohedral and sinters at a higher sintering temperature of 750 °C with $\varepsilon_r$ of 7.6 and Qf of 22,000 GHz but addition of rutile lowers the sintering temperature with improvement in microwave dielectric properties. The $0.7LiZnVO_4$–$0.3TiO_2$ ceramic sintered at 680 °C has a permittivity of 12.6, Qf of 38,000 GHz and a $\tau_f$ of 5 ppm/°C. However, it is not revealed how rutile which has a high sintering temperature can lower the sintering temperature of $LiZnVO_4$. Although, this composite has excellent microwave dielectric properties with a low sintering temperature, it reacts with Ag electrode material. The compounds rich in vanadium and niobium react with silver unlike the ones that are rich in bismuth in both V and Nb systems [26].

Among the vanadates $CaV_2O_6$ has the highest Qf of 123,000 with relative permittivity of 10.2. However, its chemical compatibility with electrode materials is not investigated. In general vanadates react with silver electrode material and Al is a possible electrode although its conductivity is lower than silver.

### 2.3. Tungstates

A large number of tungstate based materials have been reported as low loss microwave materials [43]. However, very few of them have sintering temperature suitable for ULTCC applications [43–47]. Many of the tungstate based materials in combination with molybdates have ultra-low sintering temperatures and are discussed in Section 2.4 on molybdates. $Li_2WO_4$ which has a rhombohedral crystal structure sinters at about 650 °C and has a relative permittivity $\varepsilon_r$ of 5.5 with a high Qf of 62,000 GHz. However, it has a high negative $\tau_f$ of −146 ppm/°C. It is chemically compatible with silver and aluminum conductors [43]. Fig. 8 shows the XRD pattern of $Li_2WO_4$ sintered at 600 °C and cofired with 20 wt% of silver and aluminum conductors at 640 °C. The XRD patterns show the diffraction peaks of $Li_2WO_4$, Ag and Al and there are no additional peaks reflecting formation of secondary phase. The $LiBiW_2O_8$ ceramic is monoclinic and the ceramic sintered into a dense body at 700 °C [44]. It has a relatively high permittivity of 26.5 and high quality factor of 16,400 GHz with a $\tau_f$ of −70 ppm/°C. However, $LiBiW_2O_8$ is not suitable for ULTCC applications since it easily reacts with silver electrode material. The $(Ag, Bi)_{0.5}WO_4$ is another tungstate based material, which has scheelite monoclinic crystal structure with a low sintering temperature of 580 °C. It has a relative permittivity of 35.9 with Qf of 1300 GHz and negative $\tau_f$ of 69 ppm/°C [46]. This material reacts with silver but is chemically compatible with aluminum conductors. $Li_2A_2W_3O_{12}$ (A = Mg, Zn) is another group of tungstate compounds, which can be sintered at about 700 °C [45]. $Li_2Zn_2W_3O_{12}$ does not form as a single phase material but is composed of $ZnWO_4$ and $Li_2WO_4$ with a relative permittivity of 11.3, Qf of 24,500 and $\tau_f$ of −100 when sintered at 700 °C. The $Li_2Mg_2W_3O_{12}$ is single phase and well densifies at 720 °C with a relative permittivity of 8.4, Qf of 56,700 GHz and $\tau_f$ −73 ppm/°C.

The PbO–$WO_3$ binary system has two low melting ULTCC compounds, i.e., $PbWO_4$ and $Pb_2WO_5$ [48]. The $Pb_2WO_5$ has a monoclinic crystal structures and can be well densified at a sintering temperature of 520 °C. It has a relative permittivity of 16.4, Qf of 14,800 GHz with a $\tau_f$ of −95 ppm/°C. The $PbWO_4$ has a slightly

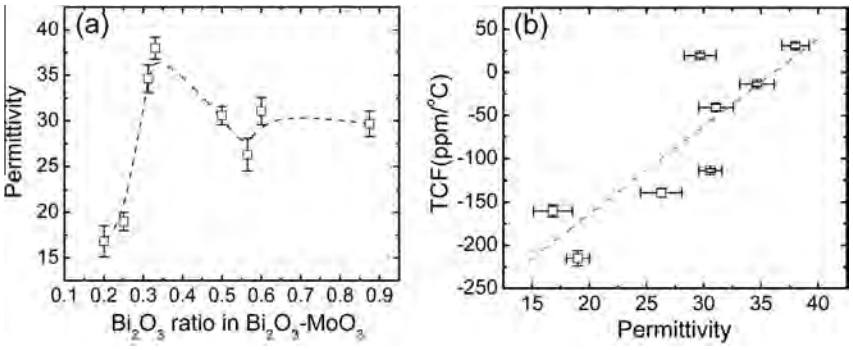


**Fig. 10.** Variation of (a) relative permittivity of $Bi_2O_3$–$MoO_3$ as a function of $Bi_2O_3$ ratio (b) $\tau_f$ as a function of permittivity (after Zhou et al. [49]).

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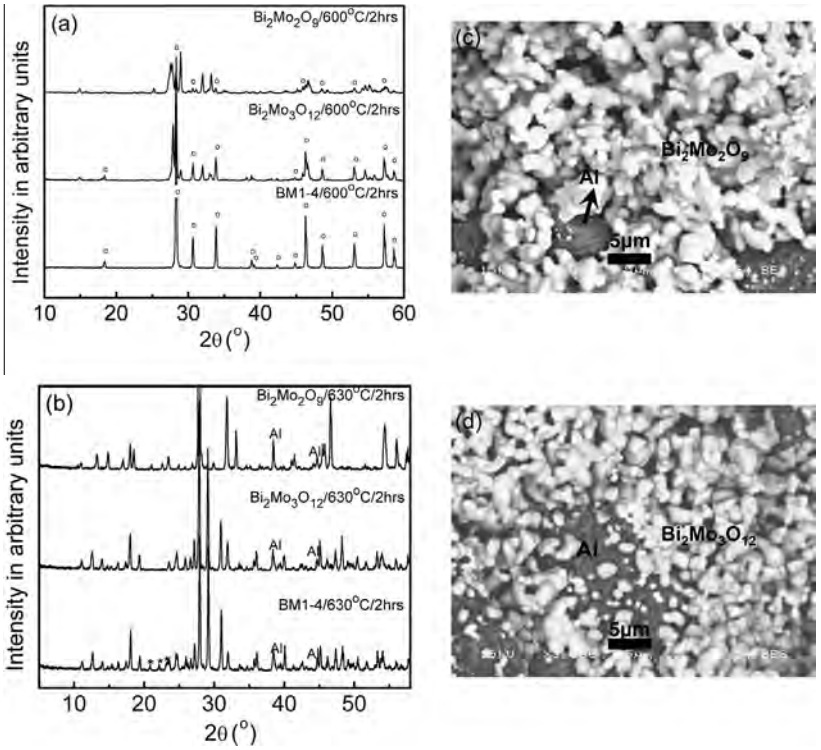


**Fig. 11.** X-ray diffraction pattern of $Bi_2O_3$–$MoO_3$ compounds (a) cofired with 20 wt% of Ag (b) 20 wt% Al at around 630 °C (O $AgBi(MoO_4)_2$, ∗ $Al_2(MoO_3)_3$ (c) SEM pictures of $Bi_2Mo_2O_9$ cofired with Al (d) $Bi_2Mo_3O_{12}$ cofired with Al (after Zhou et al. [49]).

higher sintering temperature (620 °C) and a higher relative permittivity of 21.4 with Qf of 43,000 GHz and a low $\tau_f$ of −7 ppm/°C. Fig. 9 shows the SEM microstructure of $Pb_2WO_5$ and $PbWO_4$ ceramics sintered at 520 and 620 °C for 2 h, respectively. Both the materials did not react with Ag or Al electrode materials.

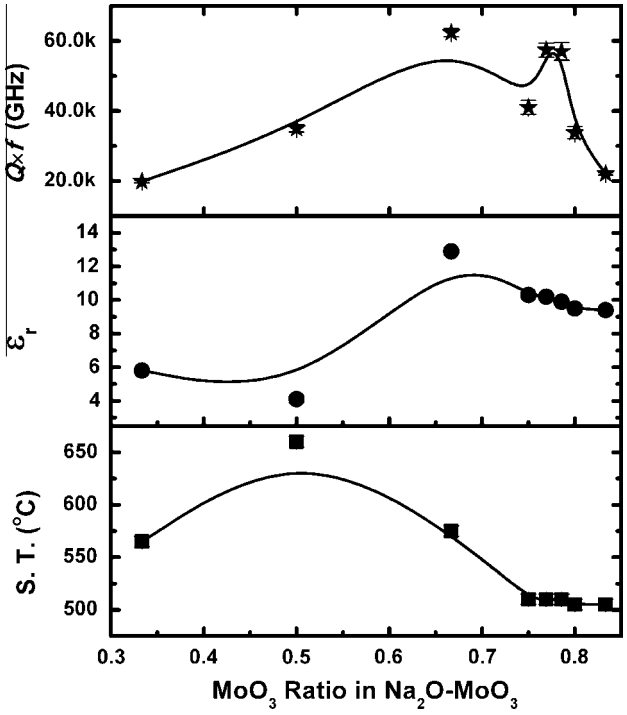


**Fig. 12.** Variation of relative permittivity, Qf and sintering temperature as a function of $MoO_3$ ratio in $Na_2O$–$MoO_3$ system (after Zhang et al. [55]).

## 2.4. Molybdates

Recently several authors reported the microwave dielectric properties of bismuth based molybdates [49–65]. Zhou et al. made a detailed study [49] of several materials in the $Bi_2O_3$–$MoO_3$ system such as $Bi_2O_3$–$4MoO_3$, $Bi_2Mo_3O_{12}$, $Bi_2O_3$–$2.2MoO_3$, $Bi_2Mo_2O_9$,

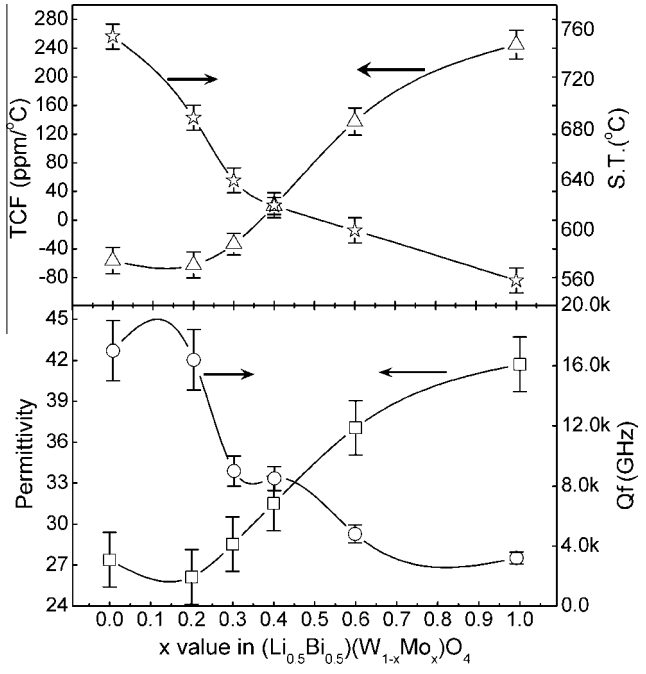


**Fig. 13.** Variation of microwave dielectric properties of $(Li_{0.5}Bi_{0.5})(W_{1-x}Mo_x)O_4$ as a function $x$ (after Zhou et al. [68]. Reproduced with permission from World Scientific Publishers).

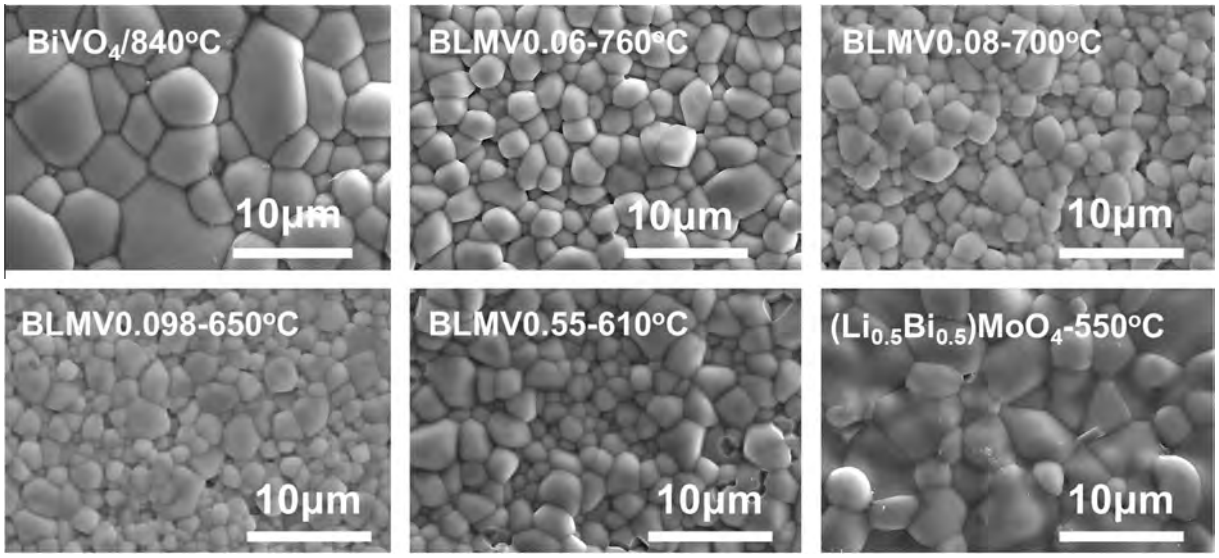


**Fig. 14.** Scanning electron microscopy photos of the $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ ceramics ($x = 0$, 0.06, 0.08, 0.098, 0.55, and 1) sintered at different temperatures but to optimal density (after Zhou et al. [67]).

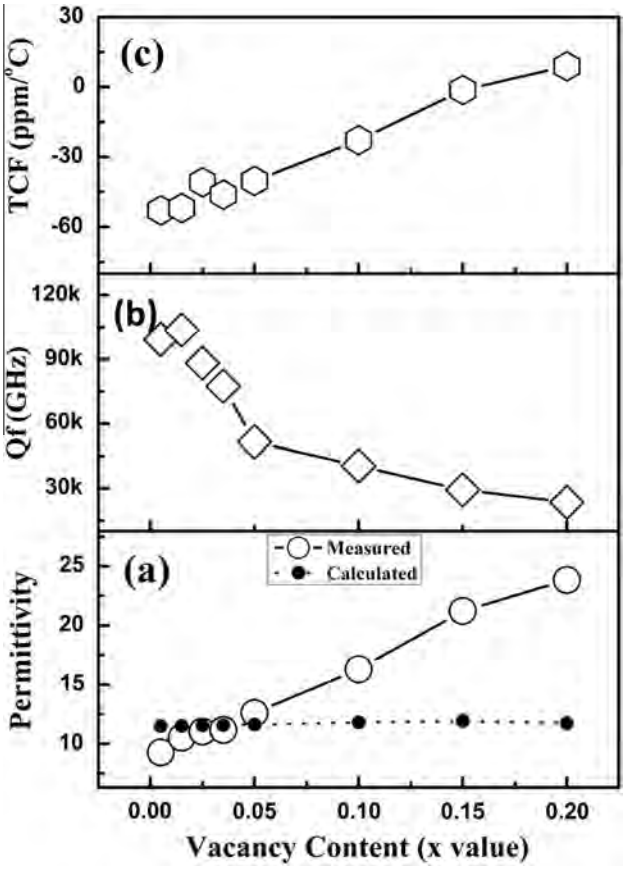


**Fig. 15.** Variation of (a) permittivities (b), Qf values (c) and $\tau_f$ values of $(Ca_{1-3x}Bi_{2x}\Phi_x)MoO_4$ ceramics as a function of $x$ value (after Guo et al. [60]).

$Bi_2MoO_6$, $1.3Bi_2O_3$–$MoO_3$, $3Bi_2O_3$–$2MoO_3$, and $7Bi_2O_3$–$MoO_3$. Many of these materials have sintering temperatures less than 700 °C and the dielectric properties are given in the supplementary file. The $Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$, and $Bi_2MoO_6$ have a monoclinic crystal structure. The $Bi_2MoO_6$, $1.3Bi_2O_3$–$MoO_3$, $3Bi_2O_3$–$2MoO_3$ and $7Bi_2O_3$–$MoO_3$ have sintering temperatures above 700 °C. Fig. 10a shows the variation of the relative permittivity of the $Bi_2O_3$–$MoO_3$ materials as a function of composition. Among the compounds in this system, $Bi_2Mo_2O_9$ has the highest relative permittivity and has positive $\tau_f$. The $\tau_f$ varies almost linearly with relative permittivity as shown in Fig. 10b. As permittivity decreases the $\tau_f$ deceases and become negative. The quality factors of these materials are in the range 9300–12,500 GHz. Chemical compatibility studies indicates that Ag reacts with these materials forming $AgBi(MoO_4)_2$ and other phases as evidenced by Fig. 11a and b. However, the materials are chemically compatible with Al. Fig. 11c shows the SEM micrograph of the $Bi_2Mo_2O_9$ and $Bi_2Mo_3O_{12}$ cofired with Al indicating the non-reactivity. It is found that partial substitution of Bi by La and Nd or doping with a small amount of $Nb_2O_5$ can considerably improve the $\tau_f$ and quality factors of $Bi_2Mo_2O_9$ [50,59]. The $Bi_2O_3$–$MoO_3$ materials have ultra-low firing temperatures, good microwave dielectric properties and chemically compatible with Al and are suitable ULTCC applications.

Zhou et al. reported [5] several ultra-low firing materials such as $Li_2MoO_4$, $Li_2Mo_4O_{13}$, $Li_3BiMo_3O_{12}$ and $Li_8Bi_2Mo_7O_{28}$ in the $Li_2O$–$Bi_2O_3$–$MoO_3$ system with useful microwave dielectric properties. These materials have relative permittivity in the range 5.5–44.4, Qf = 3000–46,000 GHz and $\tau_f$ in the range −235 to +245 ppm/°C. These compounds are found to be chemically compatible with silver and aluminum electrodes.

Recently Kahari et al. reported [52,53] novel method to prepare $Li_2MoO_4$ ceramics at room temperature by moistening the water soluble $Li_2MoO_4$ powder using deionized water and pressing under a pressure of about 130 MPa. The samples were then dried at room temperature or at 120 °C. The reference samples were also prepared by sintering at 540 °C. There was no appreciable difference in the sintered density of the samples dried at room temperature, dried at 120 °C or sintered at 540 °C. The amount of water in the pressed samples was about 2–3 wt% before drying or sintering. It is believed that the densification of the samples occurred during pressing. X-ray diffraction study showed that the crystal structure remains the same and water did not react to form any hydrates. The samples showed a relative permittivity in the range 4.6–5.2 at 9.6 GHz. The room temperature dried samples showed a Qf value of about 10,200 GHz, dried at 120 °C had 14,000 GHz and that sintered at 540 °C had 18,500 GHz respectively. This difference in dielectric properties is attributed to the presence of small amount of residual water. It was found [53] that ceramic powder

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particle size has great influence on preparation, densification and dielectric properties. Larger particles are advantageous in fabricating $Li_2MoO_4$ ceramics by moistening and pressing method. Smaller particles lead to clay like clusters leading to non-uniform densification, warpage and cracking. Kahari et al. [53] tailored the dielectric properties by adding $TiO_2$ and $BaTiO_3$ in $Li_2MoO_4$ with optimized room temperature preparation method. Further work need to be done whether this technique can be used in other water soluble systems.

Several compounds in the $Na_2O$–$MoO_3$ system with ultra-low sintering temperature in the range 500–660 °C have interesting microwave dielectric properties [55]. Three single phase compounds identified in this system are $Na_2MoO_4$, $Na_2Mo_2O_7$ and $Na_6MoO_{11}O_{36}$. All these materials sintered well with densification in the range 90–98%. These compounds have relative permittivity in the range 4–13.4, Qf up to 62,400 GHz and $\tau_f$ in the range −57 to −115 ppm/°C. Fig. 12 shows the variation of relative permittivity, Qf and sintering temperature as a function of $Na_2O$–$MoO_3$ ratio. As the $MoO_3$ fraction increases to about 0.7, the relative permittivity and quality factor increase. These compounds are chemically compatible with Al electrodes.

Substitution of several $M^{2+}$ and $M^{3+}$ (M = Ca, Zn, Al, In, Fe) for Bi in $Li_3BiMo_3O_{12}$ ceramics resulted in the significant improvement of the microwave dielectric properties [63,66]. The $Li_2Zn_2Mo_3O_{12}$, $Li_3AlMo_3O_{12}$, $Li_3InMo_3O_{12}$ have Lyonsite related crystal structure. The $Li_2Ca_2Mo_3O_{12}$ did not form and resulted in a multiphase ceramic ($Li_2MoO_4$ + $CaMoO_4$) but it has a very high quality factor of 108,000 GHz. Partial substitution of rare earth for Li in the scheelite $Li_2MO_4$ forming $(Li_{0.5}Ln_{0.5})MoO_4$ increased the dielectric constant but degraded the quality factor and $\tau_f$ [64]. Addition of $TiO_2$ is found to improve the $\tau_f$ of $Li_2MoO_4$ without much degradation of the quality factor. The $0.55Li_2MoO_4$–$0.45TiO_2$ sintered at 700 °C showed a $\tau_f$ of −5 ppm/°C with $\varepsilon_r = 10.6$ and Qf = 30,100 GHz [65]. However, addition of more than 45 mol% $TiO_2$ increased the sintering temperature to above 700 °C. Zhou and co-workers [67,68] reported simultaneous substitution of A site Li by Bi and B site Mo by W or V in $Li_2MoO_4$, which considerably increased the dielectric constant and improved the $\tau_f$ with ultra-low sintering temperatures. X-ray diffraction study revealed that $(Li_{0.5}Bi_{0.5})$ $(W_{1-x}Mo_x)O_4$ ceramic with $x \leqslant 0.3$ form a wolframite solid solution, and for $x$ = 0.4–0.6 has a mixture of scheelite and wolframite. Fig. 13 shows the variation of relative permittivity, $\tau_f$, sintering temperature and quality factor as a function of the $x$ value. The sintering temperature and quality factor decreases with $x$ value whereas the $\tau_f$ and relative permittivity increases with $x$ value. The composition $(Li_{0.5}Bi_{0.5})(W_{0.6}Mo_{0.4})O_4$ sintered at 620 °C showed a relative permittivity of 31.5, Qf of 8500 GHz and $\tau_f$ = 20 ppm/°C. X-ray diffraction analysis showed that $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ ceramics undergo a phase transition from monoclinic to scheelite tetragonal structure at $x$ close to 0.1. The phase boundary at room temperature is near the composition $x$ = 0.098. The sintering temperature decreases from 840 to 550 °C with increase in $x$ value. As $x$ increases the grain size also decreases within the monoclinic phase. Fig. 14 shows the SEM microstructure of the $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ ceramics for different $x$ values indicating the formation of single phase solid solution ceramics. The relative permittivity, quality factor and sintering temperature decrease with increase in $x$ value whereas the $\tau_f$ value increases with $x$. The composition $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ for $x$ = 0.098 shows excellent microwave dielectric properties with $\varepsilon_r$ = 81, Qf = 8000 GHz and $\tau_f$ 10 ppm/°C when sintered at 650 °C and is chemically compatible with common electrodes such as Ag and Al.

Zhou and co-workers [69–72] reported microwave dielectric properties of $(ABi)_{1/2}MoO_4$ ceramics with A = Li, Na, K, Rb, Ag, Ca, etc. All these materials can easily be sintered at temperatures below 700 °C. The microwave dielectric properties of these materials are given in the supplementary file. In general they have relatively low quality factors (less than 13,000 GHz). However, the Ca substituted composition with $x$ = 0.15 $[(Ca_{1-3x}Bi_{2x}\Phi_x)MoO_4]$ ($x$ = vacancy) has excellent properties with $\varepsilon_r$ = 21.2, Qf = 29,300 GHz, $\tau_f$ = −1 ppm/°C with sintering temperature of

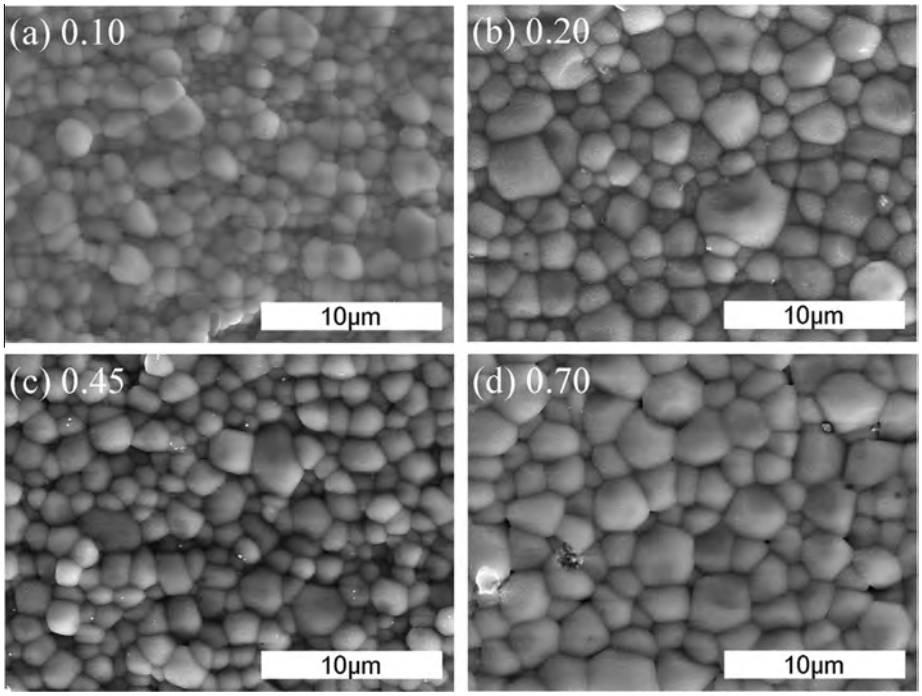


**Fig. 16.** SEM micrographs of the $x(Ag_{0.5}Bi_{0.5})MoO_4 - (1-x)BiVO_4$ ceramics: (a) $x$ = 0.10 sintered at 610 °C; (b) $x$ = 0.20 sintered at 610 °C; (c) $x$ = 0.45 sintered at 530 °C; (d) $x$ = 0.70 sintered at 530 °C (after Zhou et al. [61]. Reproduced with permission from American Chemical Society).

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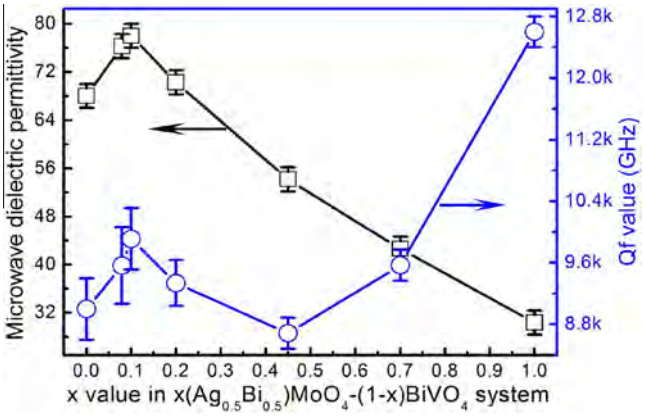


**Fig. 17.** Variation of microwave dielectric properties of the $x(Ag_{0.5}Bi_{0.5})MoO_4 - (1-x)BiVO_4$ ($0.0 \leqslant x \leqslant 1.0$) ceramics as a function of $x$ (after Zhou et al. [61]. Reproduced with permission from American Chemical Society).

700 °C. The Ca substitution results in A site vacancy. The relative permittivity and $\tau_f$ increase with $x$ but the quality factor decreases as shown in Fig. 15. All these compounds react with silver electrode material. It is found [61] that the sintering temperature of $(Ag_{0.5}Bi_{0.5})MoO_4$ could be effectively lowered from 610 °C to about 520 °C by forming a solid solution with $BiVO_4$. The scheelite monoclinic structure transforms to tetragonal scheelite at $x = 0.1$ in the $x(Ag_{0.5}Bi_{0.5})MoO_4 - (1-x)BiVO_4$ solid solution. Fig. 16 shows the SEM micrographs of the ceramics for different values of $x$ and sintered at different densification temperatures. Homogeneous and uniform microstructure with grain sizes in the range 1–3 μm is observed without any second phase. The permittivity initially increases with $x$, reaches a maximum of 78 near the phase transition composition and gradually decreases as shown in Fig. 17. The quality factor also increases with $x$ up to the phase transition point and then decreases up to $x = 0.45$ as depicted in Fig. 17. The best microwave dielectric properties are observed near the phase transition at $x = 0.1$ with $\varepsilon_r$ of about 75 and quality factor of about 9000 GHz.

The $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramics with a scheelite crystal structure can be sintered into dense ceramic at 580 °C [72]. It has good microwave dielectric properties with $\varepsilon_r = 26.3$, Qf is about 10,000 GHz and $\tau_f$ of about +20 ppm/°C. Fig. 18 shows the SEM microstructure of the ceramic sintered at 580 °C with and without Ag and Al electrode materials. A dense and homogeneous microstructure with grains of about 1–4 μm is obtained. It reacts with silver but is chemically compatible with aluminum electrode.

Zhang et al. [73] recently reported a series of ultra-low temperature sinterable compositions such as $K_2Mo_2O_7$, $K_2Mo_3O_{10}$ and $K_2Mo_4O_{13}$ in the $K_2O$–$MoO_3$ binary system. The $K_2Mo_2O_7$ has the lowest sintering temperature of 460 °C. It has a triclinic crystal structure with relative permittivity of 7.5 and Qf = 22,000 GHz. The variation of relative permittivity, Qf and $\tau_f$ with sintering temperature is plotted in Fig. 19. The microstructure of the fractured surface of the ceramics at the optimized sintering temperature is also given in the figure. All these ceramics have low sintering temperature, chemically compatible with Al electrode material, good dielectric properties, inexpensive chemicals and are suitable for ULTCC applications. However, the $\tau_f$ in the range −63 to −92 ppm/°C and need to be tailored. The $(K_{0.5}La_{0.5})MoO_4$ is another interesting material which can be densified at 660 °C exhibiting a high quality factor of about 59,000 GHz [74]. Rare earth molybdates such as $Nd_2Mo_4O_{15}$ and $Sm_2Mo_4O_{15}$ have very good quality factors (about 60,000 GHz) but their sintering temperatures are relatively high at about 690–700 °C and their $\tau_f$ are close to −50 ppm/°C [75].

Recently it was reported that silver based molybdate has very low sintering temperature [76,77]. The $Ag_2MoO_4$ can be densified at 450 °C and has relative permittivity of 8.1, Qf = 17,000 GHz and $\tau_f$ of −133 ppm/°C. It is chemically compatible with silver but reacts with Al. Partial substitution of Ag with Na further lowers the sintering temperature to 400 °C with considerable improvement in the microwave dielectric properties [77].

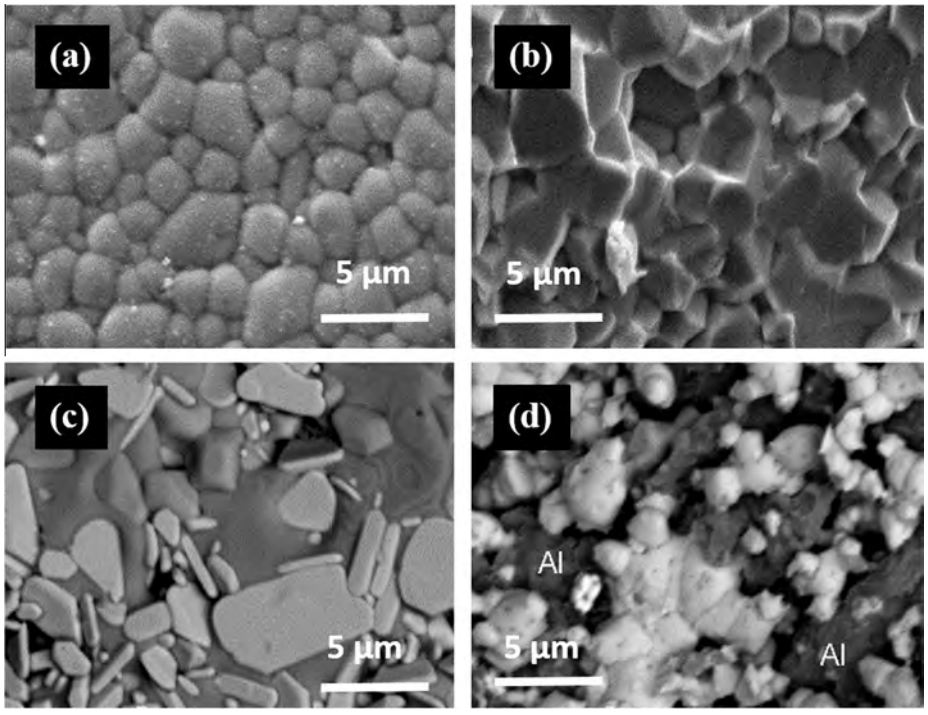


**Fig. 18.** SEM micrographs of the (a) natural surface (b) and fractured surface of $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic sintered at 580 °C/2 h and BSE photos of the cofired sample (c) with 30 wt% Ag at 600 °C/4 h and (d) with 30 wt% Al at 650 °C/4 h (after Zhou et al. [72]. Reprinted with permission from American Chemical Society).

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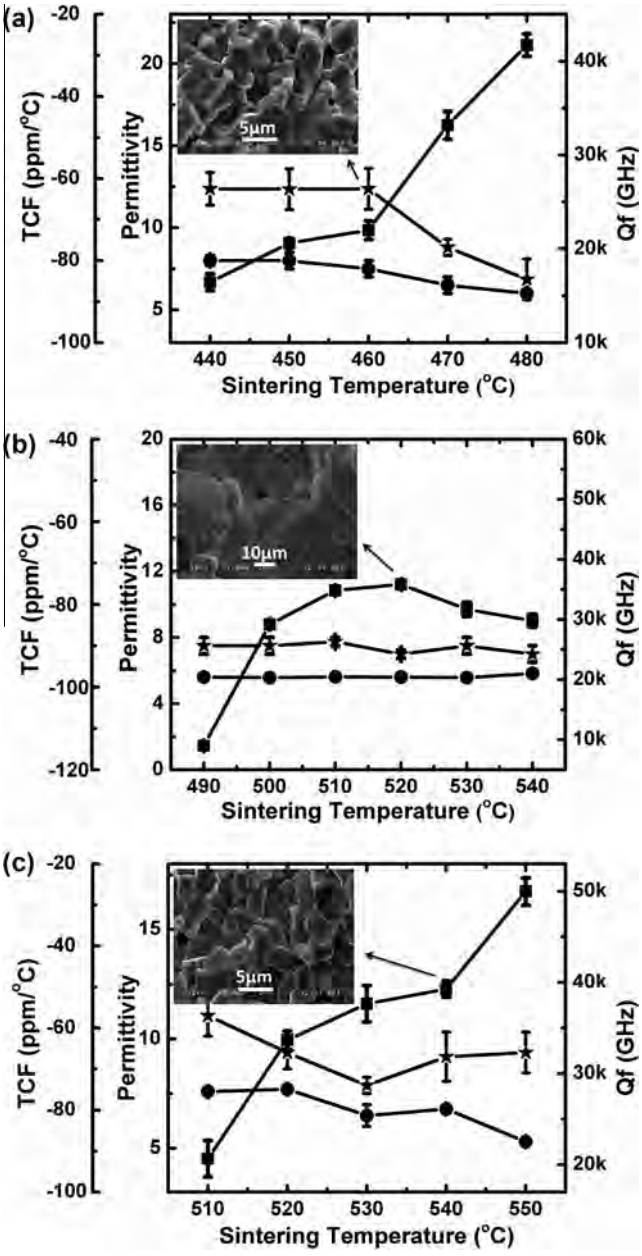


**Fig. 19.** Variation of microwave dielectric properties (■: Qf values, ●: permittivity, ★: $\tau_f$ values) of (a) $K_2Mo_2O_7$, (b) $K_2Mo_3O_{10}$, and (c) $K_2Mo_4O_{13}$ ceramics as a function of sintering temperature and SEM images of fractured surface (inserts) (after Zhang et al. [73]).

Fig. 20 shows the XRD pattern of $NaAgMoO_4$ heat treated at 350 and 400 °C and sintered with Ag and Al electrode materials. The $NaAgMoO_4$ has a spinel structure and does not react with electrode materials such as Ag and Al. Fig. 21a shows the variation of bulk density of the ceramics with sintering temperature. The ceramics starts densifying at 360 °C. The SEM picture of the ceramic sintered at 400 °C as shown in Fig. 21b reveals a uniform and homogeneous microstructure. The $NaAgMoO_4$ ceramics has the lowest sintering temperature among the reported ULTCC materials. Fig. 22 shows the variation of relative permittivity and quality factor as a function of sintering temperature. The permittivity and quality factor increase with increase in sintering temperature, reached a maximum at 400 °C and then decreased. The ceramic sintered at 400 °C exhibit a permittivity of 7.9, Qf value of 33,000 GHz and $\tau_f$ of −120 ppm/°C.

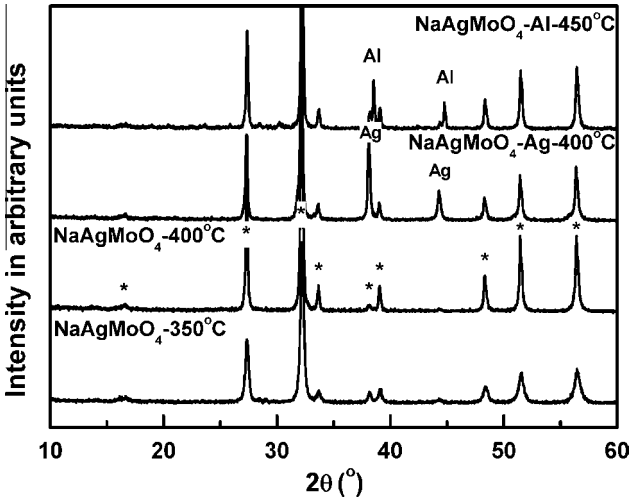


**Fig. 20.** X-ray diffraction patterns of $NaAgMoO_4$ ceramics calcined at 350 °C/4 h, 400 °C/4 h, cofired ceramic with 30 wt% Ag at 400 °C and cofired with 30 wt% Al at 450 °C (after Zhou et al. [77]. Reproduced with permission from Nature publishing group).

The $Te_2(Mo_{1-x}W_x)O_7$ is an ultra-low temperature material with interesting microwave dielectric properties [78]. It has a monoclinic structure and sinters into dense ceramic at 520 °C. Fig. 23 shows the SEM microstructure of pure and partially Mo substituted by W ceramics. The microstructure contains angular grains in the size range 2–5 μm. The pure $Te_2MoO_7$ has a relative permittivity of 13.6, Qf of 46,900 GHz and $\tau_f$ of −36 ppm/°C. Partial substitution of Mo by W improved the $\tau_f$ but degraded the quality factor. The $Te_2(Mo_{0.95}W_{0.05})O_7$ has $\varepsilon_r = 13.9$, Qf = 25,800 GHz and $\tau_f$ −13 ppm/°C.

### 2.5. Tellurates

Maeda et al. [79] were the first to report the microwave dielectric properties of a tellurate based compound ($TiTe_3O_8$). Since then several authors reported the microwave dielectric properties of several tellurate compounds [79–94]. The $TiTe_3O_8$ is difficult to densify on sintering and the samples sintered at 700 °C showed a $\varepsilon_r$ of 36 with Qf 1300 GHz and the samples sintered at 720 muffled with $TeO_2$ powder in closed alumina crucible improved the densification to 95% with $\varepsilon_r = 50$, Qf = 30,600 and $\tau_f$ of 133 ppm/°C. The microwave dielectric properties of $TeO_2$ were reported by Udovic et al. [81]. The $TeO_2$ with predominant covalent bonding is also difficult to densify and the sample sintered at 640 °C for 15 h having a porosity of 20% showed $\varepsilon_r$ of 19.3, Qf of 30,000 GHz and $\tau_f$ of −119 ppm/°C. The high negative value of $\tau_f$ has been tailored [91] close to zero by the addition of 10 wt% of $CaTiO_3$ and 15 wt% of $SrTiO_3$ by sintering at 645 and 610 °C, respectively. Although the $\tau_f$ is improved with an increase in $\varepsilon_r$, the quality factor decreased considerably to about 15,000 GHz. The addition of $CaTiO_3$ and $SrTiO_3$ to $TeO_2$ led to the formation of secondary phases $TiTeO_3$, $CaTe_2O_5$ and $SeTe_2O_5$. The $Bi_2Te_2O_8$ which has a monoclinic structure is a low loss ULTCC material. The $Bi_2Te_2O_8$ ceramic sintered in oxygen atmosphere at 650 °C for 10 h showed $\varepsilon_r$ value of 39, Qf of 23,000 GHz and $\tau_f$ of −43 ppm/°C [81]. Kwon et al. [83–85] made a detailed study on the structure and properties of materials in the $BaO–TeO_2$ system. The compounds $BaTe_4O_9$ and $BaTe_2O_6$ have low sintering temperatures with high quality factors whereas the materials $BaTeO_3$ and $Ba_2TeO_5$ have sintering temperatures above 700 °C. The $BaTe_4O_9$ sintered into dense ceramic at 550 °C and has a monoclinic crystal structure. Fig. 24 shows the variation of microwave dielectric properties as a function of sinter-

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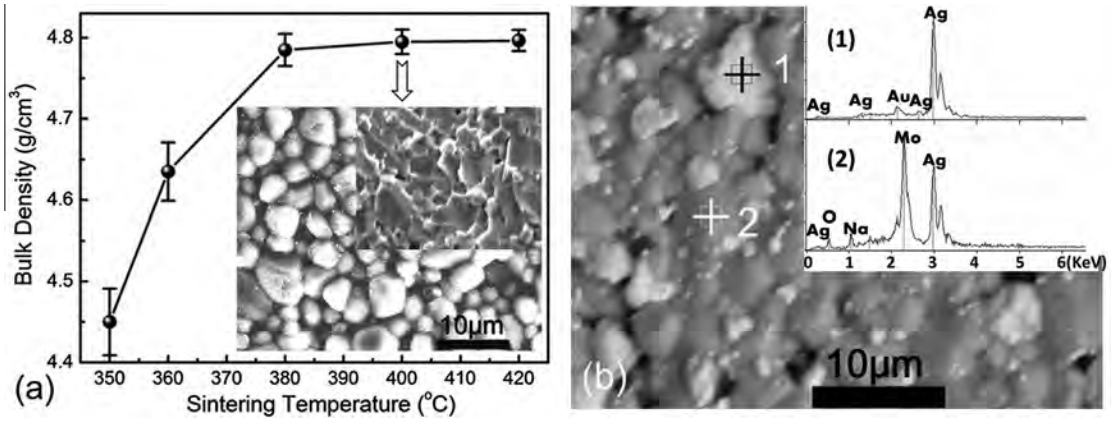


**Fig. 21.** Variation of bulk density of $NaAgMoO_4$ ceramic as a function of sintering temperature and SEM image of the ceramic sintered at 400 °C/2 h (b) BSE image of the ceramic cofired with 30 wt% Ag at 400 °C and EDS results (after Zhou et al. [77]. Reproduced with permission from Nature publishing group).

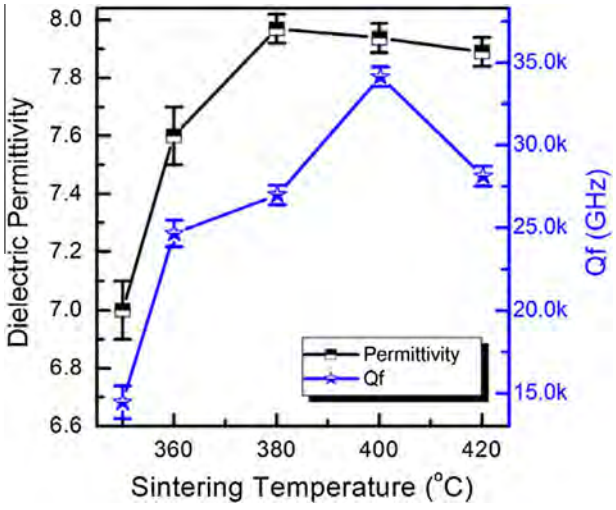


**Fig. 22.** Variation of relative permittivity and Qf value of $NaAgMoO_4$ ceramic as a function of sintering temperature (after Zhou et al. [77]. Reproduced with permission from Nature publishing group).

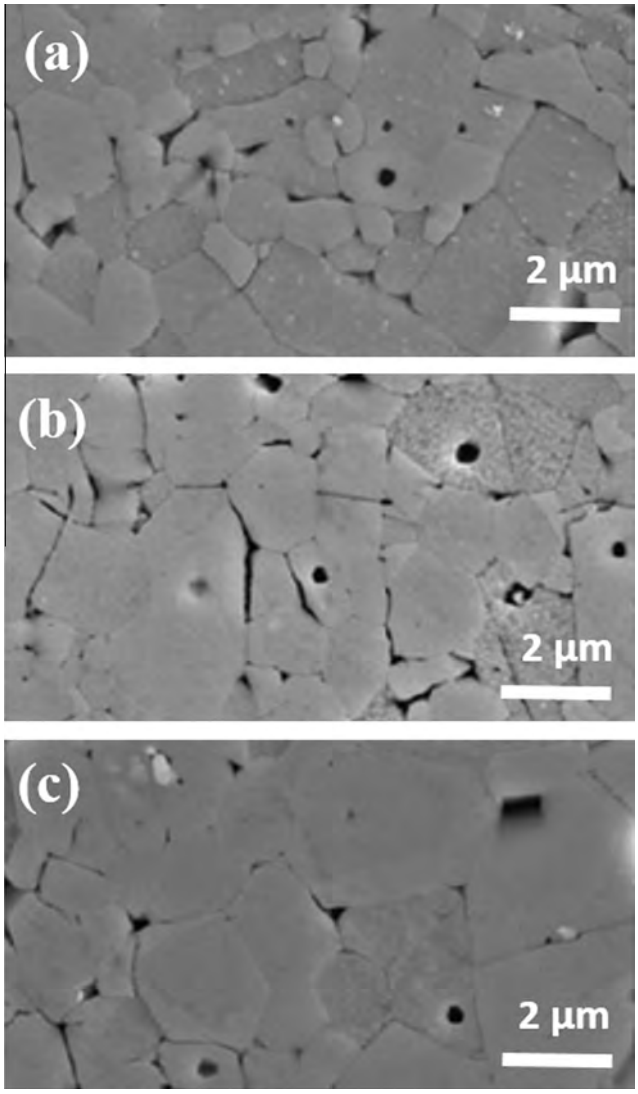


**Fig. 23.** Scanning electron microscopic micrographs of (a) $Te_2MoO_7$, (b) $Te_2(Mo_{0.95}W_{0.05})O_7$, and (c) $Te_2(Mo_{0.9}W_{0.1})O_7$ ceramics sintered at 520 °C for 2 (after Wang et al. [78]. Reproduced with permission from John Wiley & Sons).

ing temperature. The sintered $BaTe_4O_9$ has $\varepsilon_r$ of 17.5, high Qf of 54,700 GHz and $\tau_f$ of −90 ppm/°C. The ceramic is found to react with silver. However, it is compatible with aluminum electrodes. Fig. 25 shows the cross sectional microstructure of cofired $BaTe_4O_9$ with Al top electrode and integrated $BaTe_4O_9$–Al inner electrode–$BaTe_4O_9$ sample showing the chemical compatibility. The $BaTe_4O_9$ has a negative $\tau_f$ of −90 ppm/°C whereas $TiTe_3O_8$ has a relative permittivity of 50, Qf of 30,600 GHz and a positive $\tau_f$ of 133 ppm/°C. Wang et al. [91] and Jiao et al. [90] made a composite of $BaTe_4O_9$–$TiTe_3O_8$ to tailor the $\tau_f$ value. The $BaTe_4O_9$ + 40 wt% $TiTe_3O_8$ sintered at 575 °C has $\varepsilon_r$ of 25, Qf of 19,300 GHz and $\tau_f$ −3 ppm/°C [90].

Sebastian and co-workers studied [86,87,95] the structure and microwave dielectric properties of $ATe_3O_8$ [A = Sn, Zr, Zn] ceramics. The $Zn_2Te_3O_8$ has a monoclinic crystal structure and the ceramic sintered into dense body at 585 °C. The sintered ceramic has $\varepsilon_r$ = 16.2 Qf = 66,000 GHz and a $\tau_f$ of −60 ppm/°C. The high negative $\tau_f$ of $Zn_2Te_3O_8$ has been tailored by making a composite with $TiO_2$ or $TiTe_3O_8$. Addition of 4 wt% $TiO_2$ improved the $\tau_f$ to −9 ppm/°C [86,85]. However, the quality factor reduced to 27,000 GHz and the relative permittivity increased to 19.3. Addition of $TiTe_3O_8$ improved the $\tau_f$ without considerable degradation of the microwave dielectric properties [92]. The $Zn_2Te_3O_8$ + 30 wt% $TiTe_3O_8$ resulted a $\tau_f$ of 3 ppm/°C with $\varepsilon_r$ = 19.8 and Qf of 50,000 GHz. The $Zn_2Te_3O_8$ ceramic is chemically compatible with Al electrode mate-

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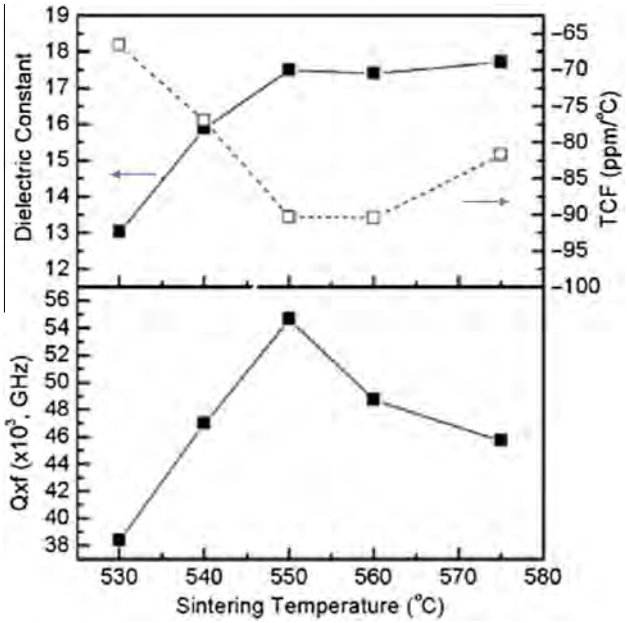


**Fig. 24.** Microwave dielectric properties of $BaTe_4O_9$ ceramics for various sintering temperatures (after Kwon et al. [83], reproduced with permission John Wiley & Sons).

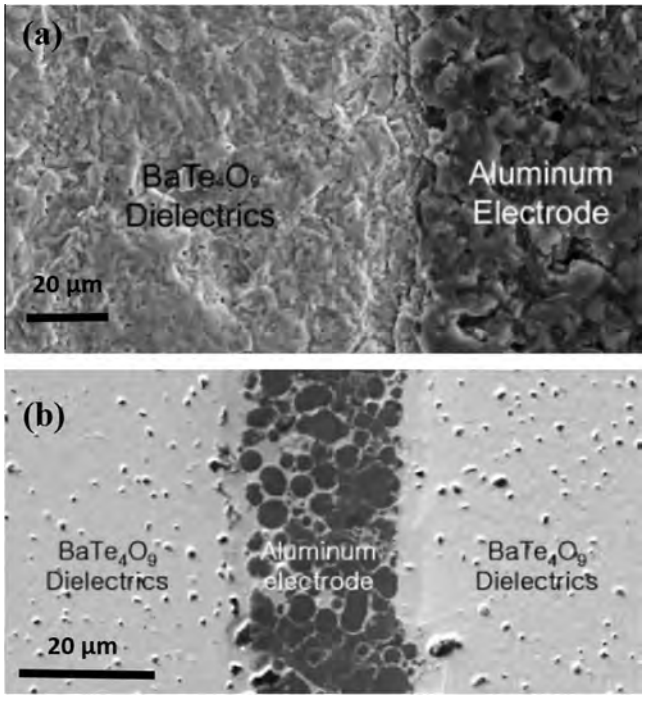


**Fig. 25.** Cross-sectional scanning electron micrographs of (a) cofired $BaTe_4O_9$ with Al top electrode and (b) integrated and cofired $BaTe_4O_9$/Al inner electrode/$BaTe_4O_9$ sample (after Kwon et al. [83]. Reproduced with permission from John Wiley & Sons).

**Table 1**
Slurry composition in tape casting (wt%) for $Zn_2Te_3O_8$ + 4 wt% $TiO_2$ (after Honkama et al. [95]).

| Powder | Ethanol + Xylene | Fish oil | PVB (B98) | Butyl benzyl phthalate (S160) | Polyalkylene glycol (UCON 50HB2000) |
|---|---|---|---|---|---|
| 62.9 | 15.4 + 15.4 | 1.3 | 3.4 | 0.8 | 0.8 |

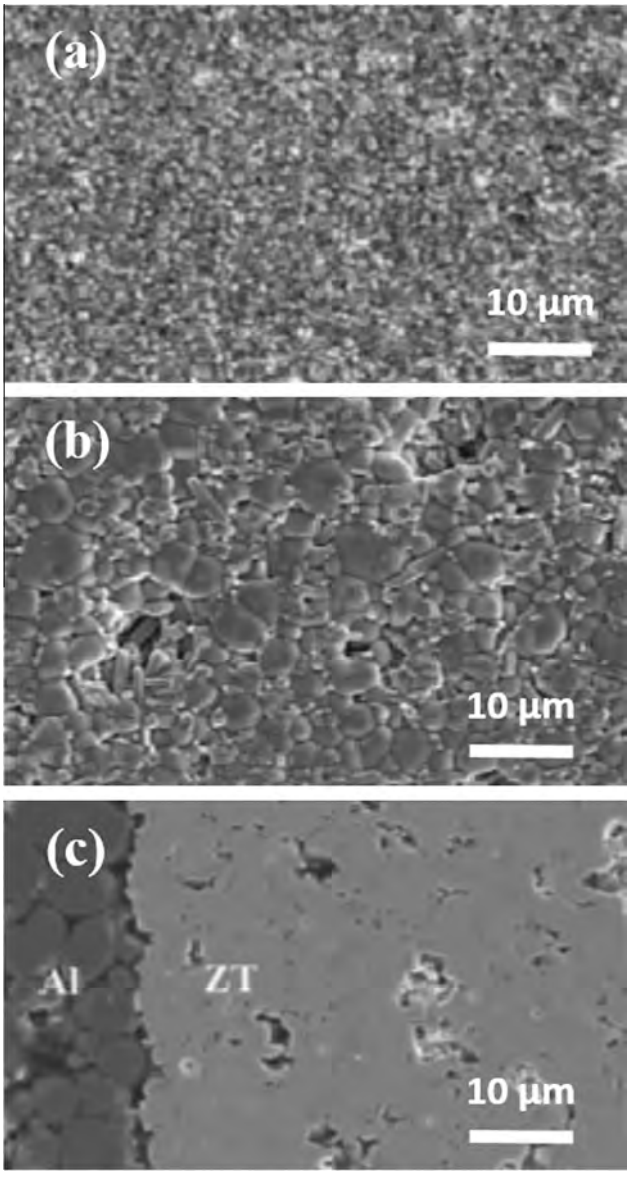


**Fig. 26.** Surface morphology of (a) green $Zn_2Te_2O_8$ + 4 wt% $TiO_2$ tapes, (b) tape sintered at 660 °C, (c) cross sectional view of the interface between ZT–Al sintered at 660 °C (after Honkamo et al. [95]).

rial [86]. Honkamo et al. [95] were the first to report tape casting of ULTCC materials. They prepared a composite of $Zn_2Te_3O_8$ + 4 wt% $TiO_2$ (ZTT) by solid state ceramic route. The ceramic powder was then mixed with solvents ethanol and Xylene and dispersant menhaden fish oil and ball milled for 24 h. The resultant slurry was further added with plasticizers butyl benzyl phthalate and polyalkylene glycol and binder polyvinyl butyral (PVB). It was then again ball milled for 24 h. The slurry composition was optimized based on several experiments on different kinds of ceramic powders with PVB based organic system [96]. It was found that a good tape casting process results green tapes with a density greater than 50% as compared to sintered full density [95,96] for easy handling and to laminate. Honkama et al. proposed [95] a relationship for the amount of organic PVB based system based as a function of specific surface area (SSA) of the ceramic powder. Based on this

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result it was found that the SSA value can give a rough estimate of the desired amounts of dispersant and binder in tape casting slurry. It was suggested that with small SSA values the amount of binder can be varied in a moderately wide range and the dispersant amount should be close to 1 wt% in relation to the ceramic powder. The slurry composition for tape casting is given in Table 1. The SSA value of the ceramic powder was 1.28 $m^2/g$. The thickness of the tape was about 80 μm and the surface roughness was about 0.1 μm.

The casted tapes were laminated with ten layers at a temperature of 70 °C and pressure 17 MPa with a dwell time of 20 min. The green density of the stack was 3.4 g $m/cm^3$, which is about 69% of the sintered density (4.9 g $m/cm^3$). The sintering temperature was optimized at 660 °C for 4 h with a linear shrinkage in plane of 14.65% and 13.7% in thickness. Fig. 26a and b shows the microstructure of the green and sintered tapes. The green tape had an average grain size of about 1 μm and the sintered tape showed a grain size of about 5 μm. The sintered ceramic is a composite containing the crystalline phases of ZTT ($Zn_2Te_3O_8$ and $TiO_2$). The ZTT is found to react with the common electrode material Ag. However, the tape when sintered with Al electrode at 660 °C did not show any reaction as revealed by Fig. 26c. The stacked and sintered tapes formed a monolithic multilayer without any trace of lamination indicating the possibility of practical application for multilayer modules. The sintered tape showed a relative permittivity of 18.2 and loss tangent 0.006 at 1 MHz. Fig. 27 shows the variation of relative permittivity and loss tangent of the sintered tape as a function of temperature in the range 0–70 °C. The loss tangent shows slight variation with temperature whereas the relative permittivity nearly remains a constant. At 7 GHz the sintered tape showed a relative permittivity of 17.3 and loss tangent of 0.0064 and are suitable for Al electrode based applications. However, the toxicity and reactivity of most of the tellurates with silver electrodes to form $Ag_6TeO_6$, $Ag_2TeO_3$ and $Ag_3Te_2O_7$ and the high cost makes them less attractive for commercial applications.

The $SnTe_3O_8$ ceramic sinters at 660 °C and the $ZrTe_3O_8$ at a much higher temperature being 760 °C [87]. The cubic $SnTe_3O_8$ has a relative permittivity of 37.3, Qf of 9600 GHz with a high positive $\tau_f$ of 223 ppm/°C. Fig. 28 shows the SEM microstructure of $SnTe_3O_8$ sintered at 660 °C revealing the formation of a dense ceramic. They tailored the high positive $\tau_f$ by making a composite with $TeO_2$ which has a negative $\tau_f$. The $MgTe_2O_5$ sinterd into dense ceramic at 700 °C [88]. Fig. 29 shows the XRD pattern of calcined and sintered $MgTe_2O_5$ revealing orthorhombic crystal structure. The $MgTe_2O_5$ has a $\varepsilon_r$ of 10.5, Qf = 61,000 GHz and $\tau_f = -45$ ppm/°C. Subodh et al. [88] investigated the microwave dielectric properties of $MgTe_2O_5$ at cryogenic temperatures. Fig. 30 shows the variation of relative permittivity and quality as a function of temperature. It is found that the relative permittivity decreased and quality factor and $\tau_f$ increased on cooling to 15 K. The ceramic showed $\varepsilon_r$ of 9.5 and quality factor of 132,000 GHz at 15 K with a high negative $\tau_f$ of 277 ppm/°C. The increase in quality factor on cooling is attributed to the decreased interaction of phonons with microwave.

### 2.6. Borates

Recently $Li_3AlB_2O_6$ ceramic, which has a triclinic crystal structure, is reported [97] as a useful ULTCC material. The microwave dielectric properties are found to depend on the sintering temperature and the degree of crystallization. Fig. 31 shows the variation of $\varepsilon_r$ and Qf as a function of sintering temperature and Fig. 32 the variation of $\tau_f$. The $\varepsilon_r$ and Qf improved with increasing sintering temperature whereas the $\tau_f$ become more negative. The degree of crystallization increases and density decreases with increase in sintering temperature. The increase in $\varepsilon_r$ and Qf is attributed to improvement in crystallization. The sample sintered at 700 °C

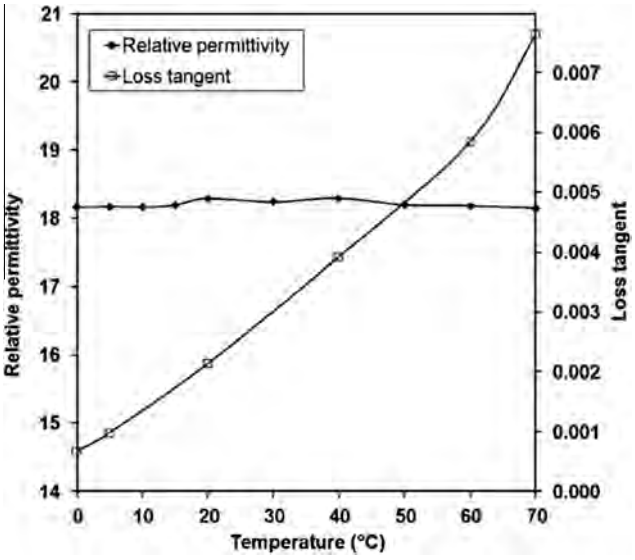


**Fig. 27.** Variation of relative permittivity and loss tangent of $Zn_2Te_3O_8$ + 4 wt% $TiO_2$ laminated tape sintered at 660 °C measured at 1 MHz (after Honkamo et al. [95]).

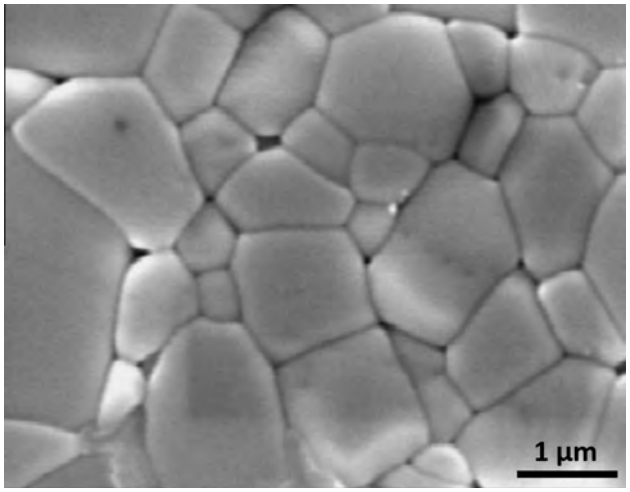


**Fig. 28.** SEM micrograph of $SnTe_3O_8$ (after Subodh and Sebastian [87]).

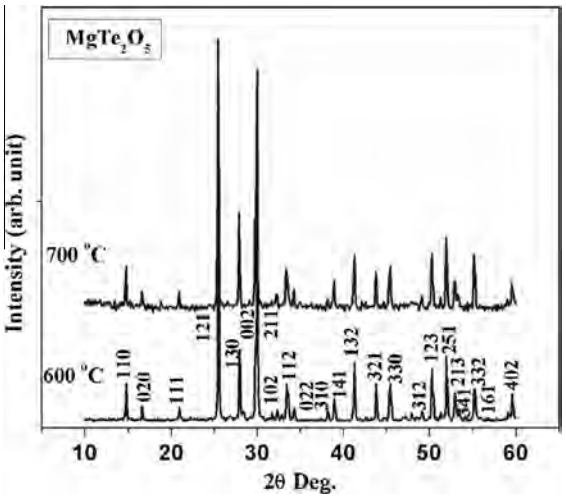


**Fig. 29.** XRD profile of $MgTe_2O_5$ calcined and sintered at 600 and 700 °C, respectively (after Subodh et al. [88]).

has $\varepsilon_r$ = 4.9, Qf = 12,600 GHz and $\tau_f$ = −201 ppm/°C. It is found that addition of 5 wt% TiB and sintered at 675 °C for 10 h considerably improved the microwave dielectric properties with $\tau_f$ of 10 ppm/°C, $\varepsilon_r$ = 4.2 and Qf = 13,000 GHz.

Chen et al. [98] made a detailed study of materials in the $Bi_2O_3$–$B_2O_3$ system and reported that two ceramics $Bi_6B_{10}O_{24}$ and $Bi_4B_2O_9$ have ultra-low sintering temperatures with interesting microwave dielectric properties. Fig. 33 shows the microstructure of sintered $Bi_6B_{10}O_{24}$ and $Bi_4B_2O_9$. The $Bi_4B_2O_9$ has a monoclinic crystal structure and the dense sample sintered at 660 °C showed a relative permittivity of 38.8, Qf of 2600 GHz and a large negative $\tau_f$ of −203 ppm/°C. The large $\tau_f$ negative value and relatively poor quality factor precludes its immediate practical application. However, Chen et al. have employed this material to lower the sintering temperature and to compensate the $\tau_f$ of $BaNd_2Ti_4O_{12}$ and $0.2CaTiO_3$–$0.8(Li_{0.5}Nd_{0.5})TiO_3$ by composite formation. The $Bi_6B_{10}O_{24}$ ceramic with orthorhombic crystal structure sintered at 700 °C has reasonably good microwave dielectric properties. It has a relative permittivity of 10.2, Qf of 10,800 GHz and $\tau_f$ of −41 ppm/°C. The reactivity of these compounds with electrode materials such as silver and aluminum has not been reported in the literature.

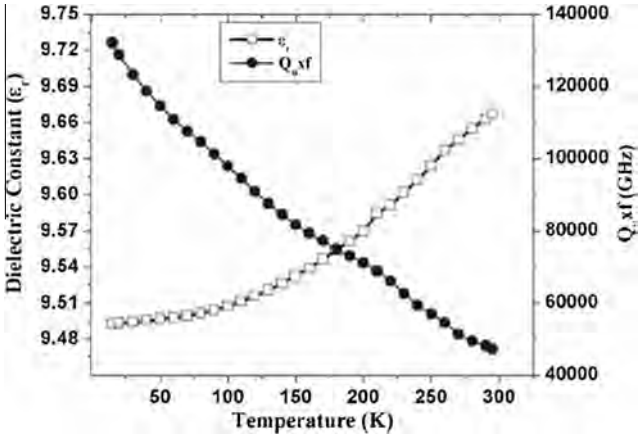


**Fig. 30.** Variation of dielectric constant and quality factor of $MgTe_2O_5$ ceramics at cryogenic temperatures (after Subodh et al. [88]).

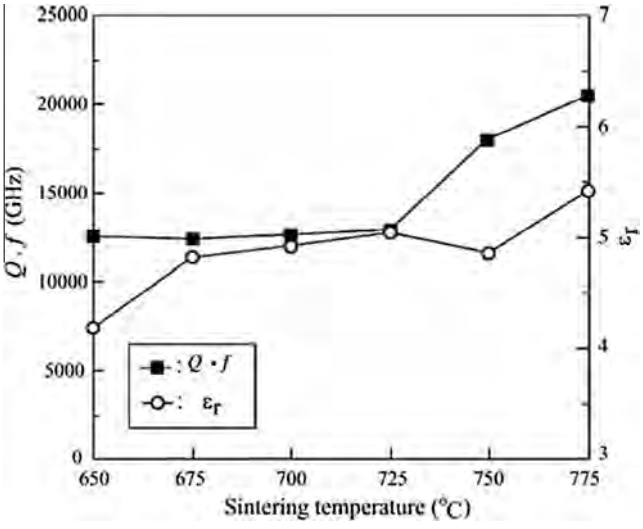


**Fig. 31.** The variation of $\varepsilon_r$ and Qf as a function of sintering temperature of $Li_2AlB_2O_6$ ceramics (after Ohashi et al. [97]. Reproduced with permission from Elsevier).

## 3. ULTCC dielectric inks

Liu et al. [99] developed screen printable $Bi_2Mo_2O_9$ dielectric inks. They prepared the ceramic by solid state ceramic route and ball milled the powder to sub-micrometer size. It was then mixed with organic vehicle in the wt% ratio 2:1 (ceramic powder: organic) to get a screen printable slurry. It was then screen printed on Al and alumina substrates to form thick films of about 15–20 μm

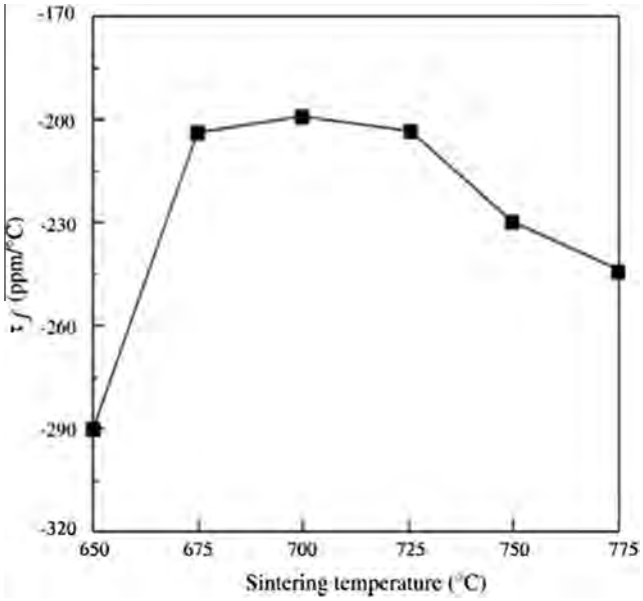


**Fig. 32.** Variation of $\tau_f$ of $Li_2AlB_2O_6$ as a function of sintering temperature (after Ohashi et al. [97]. Reproduced with permission from Elsevier).

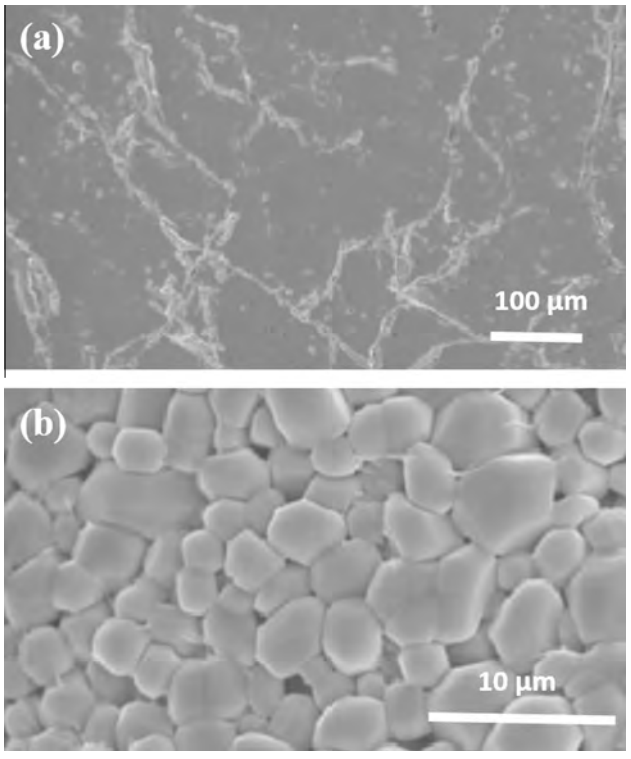


**Fig. 33.** SEM micrograph of (a) polished and thermally etched $Bi_4B_2O_9$ sintered at 660 °C/2 h, (b) fractured surface of $Bi_6B_{10}O_{24}$ ceramic sintered at 700 °C/2 h (after Chen et al. [98]. Reproduced with permission from John Wiley & Sons).

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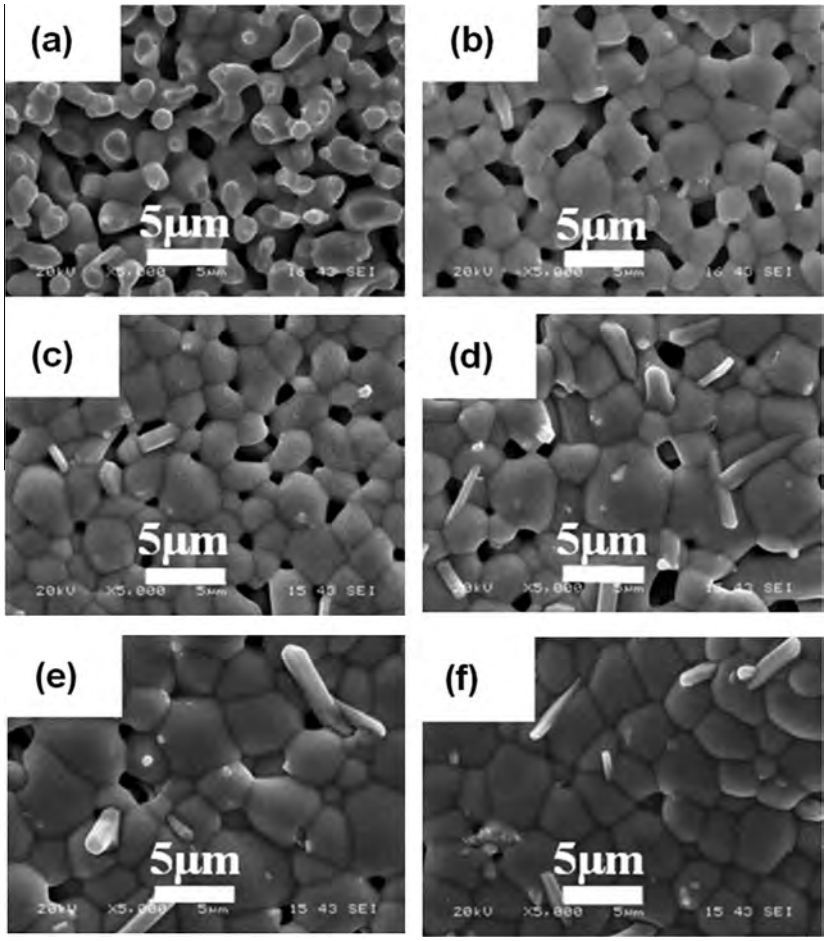


**Fig. 34.** SEM micrographs of $Bi_2Mo_2O_9$ thick films deposited on alumina substrate and sintered at different temperatures for 3 h (a) 550, (b) 580, (c) 610, (d) 630, (e) 635, (f) 645 °C (after Liu et al. [99]).

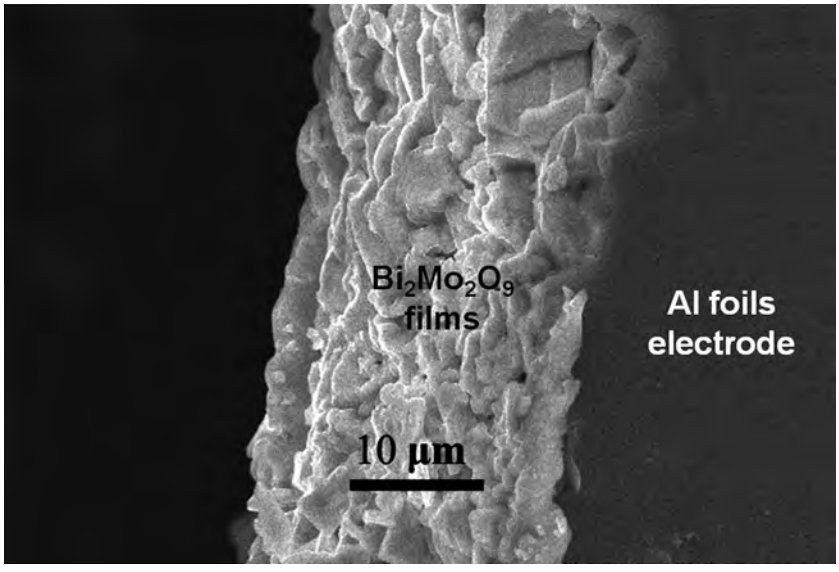


**Fig. 35.** SEM cross section micrograph of cofired $Bi_2Mo_2O_9$/Al sample sintered at 645 °C for 3 h (after Liu et al. [99]).

and sintered at different temperatures in the range 550–645 °C. Fig. 34 shows the SEM micrographs of $Bi_2Mo_2O_9$ thick films on alumina sintered at different temperatures. The thick films sintered at 645 °C showed a dense microstructure. A small amount of secondary phases are also observed which are identified as $Bi_2MoO_6$ and $Bi_2Mo_3O_2$. The $Bi_2Mo_2O_9$ thick films samples sintered at 645 °C for 3 h showed a relative permittivity of 35 with Qf of about 12,500 GHz with $\tau_\varepsilon$ of 124 ppm/°C. It was found that the $Bi_2Mo_2O_9$

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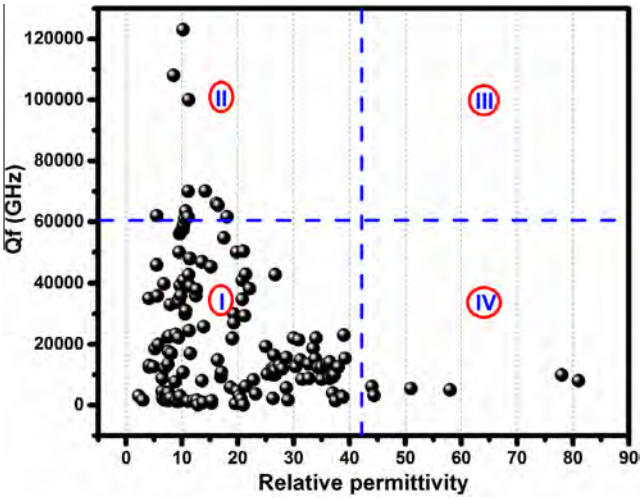


**Fig. 36.** Variation of quality factor frequency product with relative permittivity.

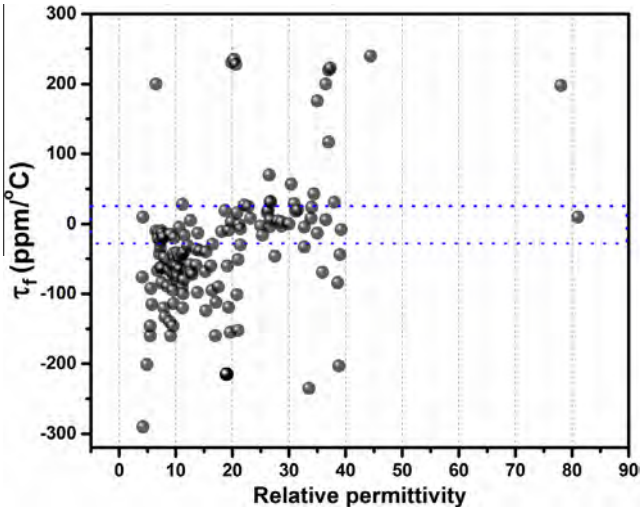


**Fig. 37.** Variation of $\tau_f$ with relative permittivity.

thick films are chemically compatible with Al electrodes as evidenced by Fig. 35 indicating the possibility of practical applications.

Recently Varghese et al. developed [100,101] screen printable and room temperature curable silica and $ZrSiO_4$ dielectric inks. The fine silica and $ZrSiO_4$ powders were made into a suitable slurry with binders, dispersants and solvents and screen printed on BoPET film substrates. The screen printed thick films are room temperature curable in a few minutes due to evaporation of solvents. The silica thick films showed a relative permittivity of 2.4–2.3 with loss tangents in the range 0.003–0.006 in the frequency range 8.2–18 GHz. The room temperature curing, low relative permittivity coupled with low loss tangent faster curing and low cost offer vast opportunities in printed electronics especially flexible electronics.

## 4. Discussion and conclusion

ULTCC materials with sintering temperature, crystal structure, relative permittivity, quality factor-frequency product, measurement frequency, temperature variation of resonant frequency and references so far reported are given in the supplementary file. The data are arranged in the order of increasing relative permittivity. In tabulating these data, we make no judgment on the measurement method and the reliability of the result. The ceramic properties such as porosity, grain size, raw materials used, measurement methods and equipment used for measurements may affect the dielectric properties and readers should be aware that exact comparison of data on materials of identical composition and manufactured in different laboratories using different processing conditions would be expected to lead to small variations in properties. The table shows about 170 ULTCC compositions with sintering temperature less than 700 °C. About 34% of ULTCC materials are based on molybdates, 25% on tellurates, about 9% contain vanadium and 5% contain tungsten. Among the ULTCC materials, $Na_2MoO_4$ ceramic has lowest $\varepsilon_r$ of 4.1, Qf of 35,000 GHz and $\tau_f$ of −76 ppm/°C with sintering temperature 660 °C [55]. $CaV_2O_6$ has the highest Qf (123,000 GHz) with $\varepsilon_r = 10.2$ and $\tau_f$ of −60 ppm/°C [40]. The $Zn_2Te_3O_8$ + 30 wt% $TiTe_3O_8$ sintered at 600 °C has the best $\tau_f$ (3 ppm/°C) with $\varepsilon_r$ of 19.8, Qf of 50,000 GHz [92]. $BaTiTe_3O_9$ has the highest negative $\tau_f$ (−372 ppm/°C) with $\varepsilon_r$ of 29.0, Qf = 1700 GHz [84]. $(Li_{0.5}Bi_{0.5})MoO_4$ has the highest positive $\tau_f$ (240 ppm/°C) with $\varepsilon_r$ of 44.4 and Qf of 3200 GHz [48]. $[(Li_{0.5}Bi_{0.5})_xBi_x][Mo_xV_{1-x}]$ with $x = 0.098$ has the highest $\varepsilon_r$ among the crystalline ULTCC materials [51]. The BBSZ + 50 wt% $BaTiO_3$ glass–ceramic sintered at 450 °C has the highest $\varepsilon_r$ (136) with $\tan\delta = 0.02$ at 100 MHz [22].

As expected the reported quality factors of the microwave dielectric ceramics decrease significantly with increasing relative permittivity as shown in Fig. 36. Most of the ULTCC materials have $\varepsilon_r < 40$ with moderate Qf as shown in Region I of Fig. 36. The Qf of the materials with $\varepsilon_r > 40$ are relatively small. There are only a handful of materials with Qf > 50,000 GHz as revealed by Fig. 36. In general the $\tau_f$ is found to increase with increasing relative permittivity as shown in Fig. 37. It is evident from Fig. 37 that most of the ULTCC materials negative $\tau_f$. However, there are reasonable number of materials with $\tau_f$ close to zero and most of these materials have $\varepsilon_r$ in the range 5–40. Fig. 38 shows the variation of relative permittivity, quality factor and $\tau_f$ as a function of sintering temperature of the ceramics. The room temperature curable dielectric inks and samples prepared at room temperature by moistening and pressing are excluded in Fig. 38. Most of the ULTCC materials have sintering temperature >600 °C and they have relatively large $\varepsilon_r$ (Fig. 38a). There are a good number of materials with $\tau_f$ close to zero with sintering temperature in the range 500–700 °C (Fig. 38c).

There are several polymers or polymer ceramic composites with very low loss factor in the microwave frequency range, which can be prepared at temperatures lower than 400 °C. However, they have very low relative permittivity, low thermal conductivity and high thermal expansion coefficient. Hence discussion on polymer based composites is not included in the present review. For this the readers are referred to the recent review in Ref. [102].

There is an urgent need for electroceramic compositions feasible for co-firing with organic or semiconductive structures expecting sintering temperatures less than 700 °C using aluminum or less than 400 °C using nano silver ink electrodes. In semiconductors, metal electrode should be deposited on top of the dielectric layers with low temperature process. Multilayer packages made by LTCC technology but with much lower sintering temperature would enable co-firing of semiconductor devices into the package. In the recent decade several electroceramic compositions with sintering temperature below 700 °C have been reported as given in the supplementary file. These materials fall in two categories. The first one (category-II) covers compositions having sintering temperature in the range 400–700 °C. This category is justified since in these temperatures only Al, Pd, or different metal mixture electrodes with relative low conductivity can be used. These ULTCC-II

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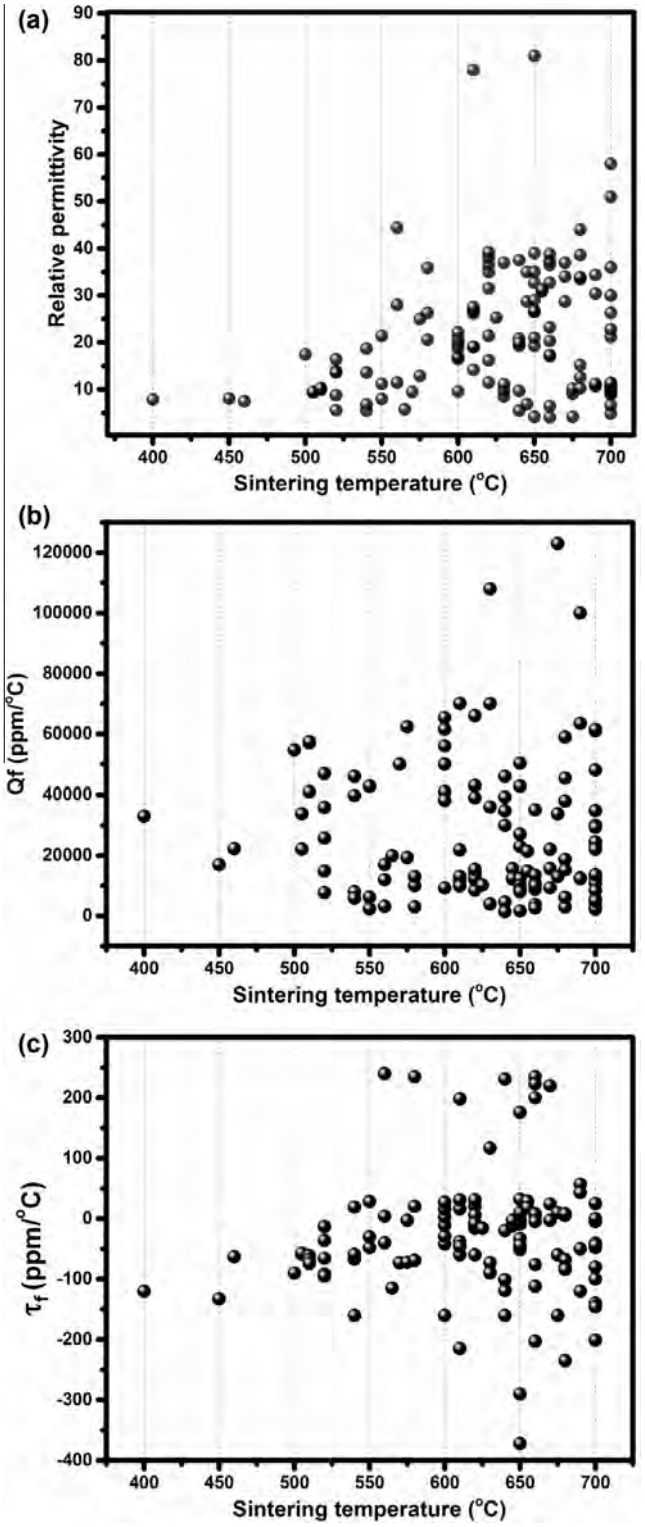


**Fig. 38.** Variation of microwave dielectric properties as a function of sintering temperature (a) $\varepsilon_r$, (b) Qf, (c) $\tau_f$.

category materials can be used on some metal, glass or ceramics substrates, but their feasibility for real multilayer applications is somewhat limited although there are many interesting compositions like $Li_2Mo_4O_{12}$ sintered at 630 °C has Qf of 108,000 GHz with $\varepsilon_r$ = 8.8 and $\tau_f$ = −89, $CaV_2O_6$ with $\varepsilon_r$ = 10.2 has a high quality factor of 123,000 GHz with $\tau_f$ = −60 ppm/oC, $Zn_2Te_3O_8$ + 30 wt% $TiTe_3O_8$ sintered at 610 °C has the best $\tau_f$ of 3 ppm/°C with $\varepsilon_r$ = 19.8 and Qf = 50,000 GHz, $[(Li_{0.5}Bi_{0.5})_xBi_x][Mo_xV_{1-x}]O_4$ with $x$ = 0.098 when sintered at 650 °C has the highest $\varepsilon_r$ of 81 with Qf of 8000 GHz, $\tau_f$ of 10 ppm/°C. $Na_2MoO_4$ with $\varepsilon_r$ = 4.1 with Qf = 35,000 GHz and $\tau_f$ = −76 ppm/°C. The main application areas can be found at moderately low frequency areas. Important application fields could be multilayer capacitors and packages.

The category-I (ULTCC-I), with sintering temperature at 400 °C or below, should be feasible with commercially available highly conductive nano silver inks in co-firing. These compositions have inherently ultra-low sintering temperatures. Although only very few compositions so far belonging to this category are reported, they will in the future provide great opportunities with integrated applications with semiconductor devices or on organic substrates. The $NaAgMoO_4$ has a low sintering temperature of 400 °C among the reported materials category-I. It has a relative permittivity of 7.9 with Qf of 33,000 GHz and $\tau_f$ of −120 ppm/°C [77]. But more recently room temperature preparation of water soluble materials by moistening and pressing has been reported [52,53] with reasonably good dielectric properties. Room temperature curable dielectric inks have also been reported [100,101]. These reports on room temperature preparation are expected to open up new applications. The room temperature preparation of water soluble dielectrics by moistening and pressing technique offer great opportunities in future [52,53]. One challenge with the ULTCC-I materials is that most of them are based on vanadates and molybdates are soluble in water. This means the ultimate device needs suitable encapsulation. These materials need to be tape casted for practical applications. In addition the low sintering temperature causes extra challenge in tape casting meaning that suitable binders, dispersants and plasticizers which can burn out before shrinkage need to be addressed. The research and development of ULTCC-I materials are still however in their initial stage. There is an urgent need for developing materials with sintering temperature less than 400 °C for future applications.

Attempts should be also done to lower the cost of production of microwave materials with emphasis on use of environment friendly materials with the possibility of recycling. In the near future, the new emerging communication applications like 5G network machine-to-machine connection and Internet of Things (IoT) will need novel dielectric ceramics with feasible component fabrication technologies. This means that the low loss ULTCC microwave ceramics will continue to be an active area of research in years to come. The future will show their importance for improved performance with cost efficient and miniaturized devices.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cossms.2016.02.004.

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