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Low temperature sintering and microwave dielectric properties of $Ce_2(WO_4)_3$ ceramics

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Abstract

$Ce_2(WO_4)_3$ ceramics have been synthesized by the conventional solid-state ceramic route. $Ce_2(WO_4)_3$ ceramics sintered at 1000 °C exhibited $\varepsilon_r = 12.4$, $Qxf = 10{,}500$ GHz (at 4.8 GHz) and $\tau_f = -39$ ppm/°C. The effects of B_2O_3, $ZnO–B_2O_3$, $BaO–B_2O_3–SiO_2$, $ZnO–B_2O_3–SiO_2$ and $PbO–B_2O_3–SiO_2$ glasses on the sintering temperature and microwave dielectric properties of $Ce_2(WO_4)_3$ were investigated. The $Ce_2(WO_4)_3$ + 0.2 wt% ZBS sintered at 900 °C/4 h has $\varepsilon_r = 13.7$, $Qxf = 20{,}200$ GHz and $\tau_f = -25$ ppm/°C.

Keywords: A. Powders: solid state reaction; B. Electron microscopy; C. Dielectric properties; E. Substrates

1. Introduction

The development of microwave dielectric materials for applications in communication systems, such as cellular phones, wireless local area networks, direct broadcasting satellite (DBS) and global positioning systems, has evolved in an unprecedented path for the last decade [1,2]. The study of microwave dielectric materials with a low relative permittivity (ε_r) and high Qxf has increased because of the need to use them as the advanced substrate materials in microwave integrated circuits (MIC) [3,4]. Moreover, the extension of the carrier frequency from industrial, scientific and medical (ISM) bands to the millimeter wave range is expected in the near future as the research on ultrahigh-speed communication systems is currently underway. These substrate materials need to have a low ε_r value ($5 \leq \varepsilon_r \leq 14$), in order to minimize the cross-coupling effect with conductors, and a high quality factor (Qxf) to increase their selectivity. A near zero temperature coefficient of resonant frequency is also required in order to ensure the stability of the frequency against temperature changes. The rapid development in the electronic industry using dielectric materials paved way for low temperature sintered substrate materials. In the multilayer structures, the sintering temperature of the dielectric materials has to be lowered below 950 °C in order to co-fire with highly conductive embedded electrodes such as Ag (melting point of Ag is 961 °C). Most of the low loss dielectrics have sintering temperatures above 1300 °C. Basically, three main approaches are adopted to lower the sintering temperature of ceramics: (i) low melting point glass addition [5,6] or addition of low melting compounds such as CuO, V_2O_5, B_2O_3 [7,8]; (ii) using starting materials with smaller particle size [9] and (iii) development of novel glass free low temperature sinterable dielectric ceramics [10]. Liquid phase sintering with glass additives is the least expensive process among the above cited methods. Recently a number of new glass–ceramic composites with low permittivity have been developed for substrate applications [11–14]. Wu and Huang [15] reported the microwave dielectric properties of various borosilicate glasses. Multicomponent glasses are more effective than single component glasses to lower the sintering temperature [16].

Several researches on compound formation in rare earth tungstates have been reported [17,18]. McCarthy et al. [19] prepared and identified many compounds in the $R_2O_3–WO_3$ system by varying the ratio of R_2O_3 and WO_3 (R = rare earth element and Y). The system based upon Ce_2O_3 is difficult because of the instability of Ce_2O_3. Yoshimura et al. [20] identified stable phases in the $Ce_2O_3–WO_3$ system. The subsolidus phase relation is also discussed for the ternary system $CeO_2–Ce_2O_3–WO_3$. Borchardt [21] reported that

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Table 1
Physical and electrical properties of glasses.

Glass code	Composition	Density (g/cm^3)	Softening temperature (°C)	ε_r	tan δ	Refs.
B	B_2O_3	2.46	450	2.5	5.5×10^{-3} (1 MHz)	[15]
ZB	$50ZnO:50B_2O_3$	3.61	610	6.9	9.4×10^{-3} (16 GHz)	[16]
BBS	$30BaO:60B_2O_3:10SiO_2$	3.40	627	7.2	4.4×10^{-3} (15 GHz)	[16]
ZBS	$60ZnO:30B_2O_3:10SiO_2$	3.60	582	7.5	10.7×10^{-3} (15 GHz)	[16]
PBS	$40PbO:20B_2O_3:40SiO_2$	12.11	442	12.1	0.01 (1 MHz)	[16]

$Ce_2O_3 \cdot 3WO_3$ is the only one compound which is produced by the reaction between CeO_2 and WO_3 in air. Recently Anjana et al. [22] reported the microwave dielectric properties of CeO_2–WO_3–TiO_2 ceramics as $\varepsilon_r = 17.0$, $Qxf = 45{,}550$ (in vacuum) and $\tau_f = 7$ ppm/°C. The structure of $Ce_2(WO_4)_3$ is monoclinic [20]. In this paper we report the synthesis, characterization and microwave dielectric properties of $Ce_2(WO_4)_3$ ceramics. The effect of B_2O_3 and borosilicate glass frits addition on the sintering behaviour and microwave dielectric properties of $Ce_2(WO_4)_3$ ceramic is also investigated.

2. Experimental procedure

The $Ce_2(WO_4)_3$ ceramic was prepared by the conventional solid-state ceramic route. High purity chemicals CeO_2 (IRE, 99.99%) and WO_3 (Aldrich, 99.9%) were used as the starting powders. Stoichiometric proportions of the chemicals were weighed and ball milled for 24 h using zirconia balls in distilled water media. The slurry was dried and then calcined for 8 h at 925 °C. The calcined powders were then ball milled for 24 h. The finely ground calcined powder so obtained was then pressed into disc shaped pucks of 20 mm diameter and about 10 mm height at a pressure of about 120 MPa using a WC die. The green compacts were fired at a rate of 5 °C/min up to 600 °C and soaked at 600 °C for 30 min to expel the binder. The pellets were then sintered in air at temperatures in the range 975–1025 °C and the dwell time was 4 h. After sintering, the samples were allowed to cool down to room temperature at a rate of 3 °C/min.

The glass powders used in this investigation were B_2O_3 (abbreviated as B), ZnO–B_2O_3 (ZB), BaO–B_2O_3–SiO_2 (BBS), ZnO–B_2O_3–SiO_2 (ZBS), PbO–B_2O_3–SiO_2 (PBS). For synthesizing glasses, high purity (Aldrich, 99.9%) oxides/carbonates were weighed stoichiometrically and mixed for 2 h in an agate mortar with pestle using distilled water as the medium. It was then melted in a platinum crucible above their softening temperature (see Table 1), quenched and powdered.

The calcined $Ce_2(WO_4)_3$ powder is subsequently mixed with different wt% of different glasses. The mixed powders were then dried and PVA was added as a binder. It was then ground well and granulated before pressing into pellets. The pellets were sintered at 850–950 °C in air for 4 h. The samples were then polished to remove the surface irregularities.

The bulk densities of the sintered samples were measured using the Archimedes method. X-ray diffraction patterns were recorded from powdered samples using CuKα radiation (Philips X-Ray Diffractometer). The sintered samples were thermally etched for 20 min at a temperature of about 25 °C below the sintering temperature and the surface morphology was studied using a scanning electron microscope (Jeol JSM-5600LV). Dielectric properties at microwave frequencies were measured by the resonance method using a Vector Network Analyzer (Agilent 8753 ET, Agilent Technologies, Palo Alto, CA). The specimen was placed on a low loss quartz spacer of height 8 mm inside a copper cavity of inner diameter 60 mm and height 46 mm whose inner side was silver plated. The use of low loss single crystal quartz spacer reduces the effect of losses due to the surface resistivity of the cavity. The $TE_{01\delta}$ mode was used for the microwave measurements [23]. The coefficient of temperature variation of resonant frequency was measured by noting the temperature variation of $TE_{01\delta}$ resonant mode at every 2 °C interval in the temperature range 25–70 °C. Usually three samples were prepared in a batch corresponding to a particular composition and the measurements were made at least twice per each specimen. The error in ε_r was calculated using the root sum of squares (RSS) method. The accuracy of ε_r measurement was restricted to the accuracy in measurement of resonant frequency and dimensions of the sample. The possible error in the measurement of permittivity was of the order of 0.3%. The uncertainty in the quality factor using $TE_{01\delta}$ mode cavity method with optimized enclosure was of the order of 3%. The errors in unloaded Q and τ_f were calculated using RSS method [1].

3. Results and discussion

The synthesizing conditions such as calcination temperature, sintering temperature and their durations were optimized for $Ce_2(WO_4)_3$ and glass added $Ce_2(WO_4)_3$ ceramic to obtain the highest density and dielectric properties. The dielectric properties of all the glasses used in this investigation have been reported [15,24] earlier and hence we synthesized those compositions, which exhibited relatively good dielectric properties at microwave frequencies (see Table 1).

Fig. 1(a) shows the variation of relative density with calcination temperature for $Ce_2(WO_4)_3$ ceramic. The relative density increases and reaches a maximum at a calcination temperature of 925 °C and then decreases for $Ce_2(WO_4)_3$ ceramic. The variation of relative density with sintering temperature for $Ce_2(WO_4)_3$ ceramic is shown in Fig. 1(b). The relative densities range from 76 to 90% for $Ce_2(WO_4)_3$ ceramic. The maximum relative density of 90% is obtained for $Ce_2(WO_4)_3$ ceramic calcined at 925 °C/8 h and at a sintering temperature of 1000 °C/4 h (theoretical density = 6.78 g/cm^3) [25]. The relative density decreased with further increase in sintering temperature.

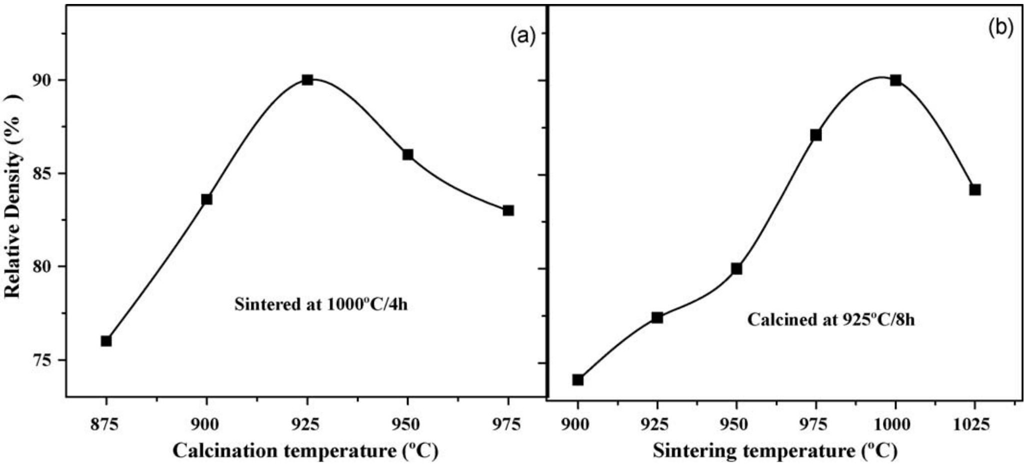

Fig. 1. Variation of relative density of $Ce_2(WO_4)_3$ ceramic with (a) calcination temperature and sintered at 1000 °C/4 h, (b) samples calcined at 925 °C/8 h and sintered at different temperatures for 4 h.

Fig. 2 shows the powder X-ray diffraction pattern of $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C for 4 h. The powder pattern of $Ce_2(WO_4)_3$ ceramic exhibits a single phase nature with monoclinic symmetry in agreement with ICDD file card number 85-0143. All peaks are indexed and the unit cell parameters are $a = 7.813$ Å, $b = 11.720$ Å and $c = 11.580$ Å with space group *C*2/*c* [15]. A SEM micrograph of $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C for 4 h is shown in Fig. 3. The SEM studies on $Ce_2(WO_4)_3$ ceramic show that the average grain size is about 10–25 µm. Microcracks are observed in the micrograph which resulted in lowering the density and thereby the percentage density of the $Ce_2(WO_4)_3$ ceramic.

The variation of microwave dielectric properties of $Ce_2(WO_4)_3$ ceramic with sintering temperature is shown in Fig. 4. The relative permittivity is corrected for porosity using the following equation derived by Penn et al. [26].

$$(\varepsilon_r)_o = (\varepsilon_r)_{cor}\left(1 - \frac{3P((\varepsilon_r)_{cor} - 1)}{2(\varepsilon_r)_{cor} + 1}\right) \tag{1}$$

where $(\varepsilon_r)_o$ is the measured relative permittivity of $Ce_2(WO_4)_3$ which contains a fractional porosity P and $(\varepsilon_r)_{cor}$ is the porosity corrected relative permittivity of the dielectric. The relative permittivity increases with sintering temperature up to a maximum of 12.4 at 1000 °C and decreases on sintering further at higher temperatures. The increase in relative permittivity is due to the increase in relative density. The relationship between relative permittivity and sintering temperature shows the same trend as that of relative density and sintering temperature (Fig. 4(a)). With increase in sintering temperature, *Qxf* increases, reaches a maximum value and thereafter decreases. The variation in *Qxf* is also consistent with the variation in relative density. Fig. 4(b) shows the variation of *Qxf* with sintering temperature of $Ce_2(WO_4)_3$. The maximum *Qxf* of 10,500 GHz is obtained by sintering at 1000 °C. At sintering temperatures below and above 1000 °C, the microwave quality factors are low due to the poor relative density of samples. Fig. 4(b) shows the influence of sintering temperature on the τ_f values of $Ce_2(WO_4)_3$ sample. The τ_f values ranged from −60 to −34 ppm/°C for the $Ce_2(WO_4)_3$ samples sintered in the temperature range of 900–1025 °C.

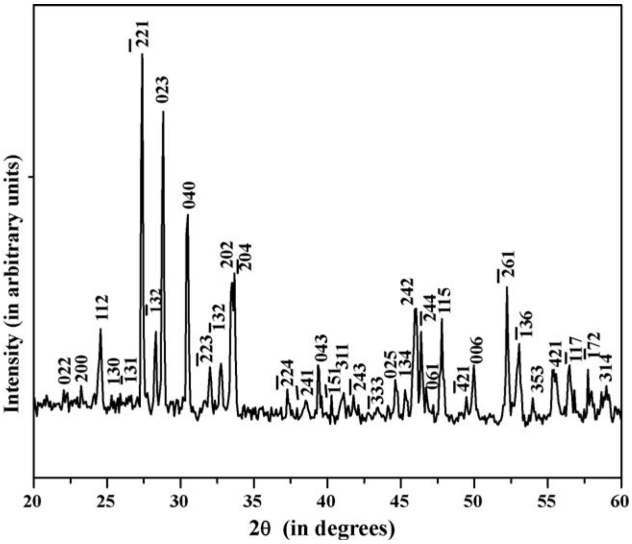

Fig. 2. X-ray diffraction pattern of $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C/4 h.

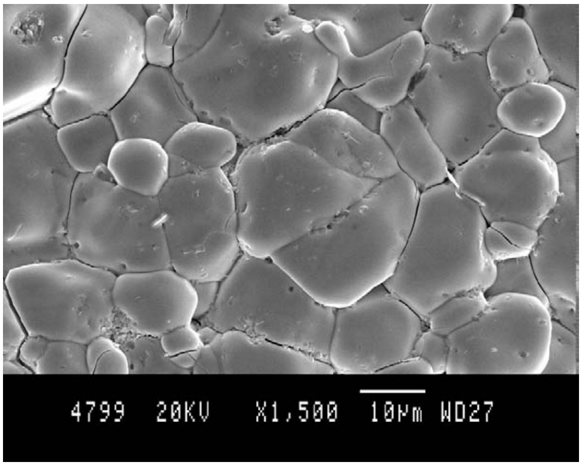

Fig. 3. SEM micrograph of $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C/4 h.

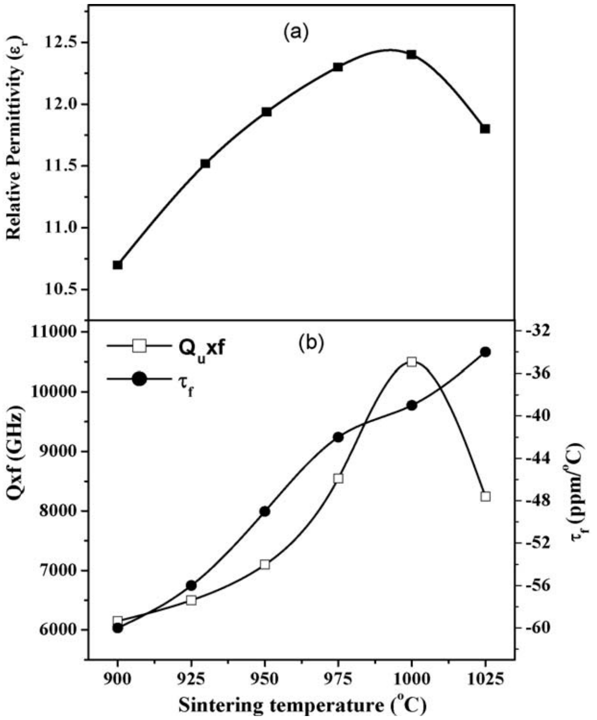

Fig. 4. Variation of microwave dielectric properties of $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C/4 h (a) ε_r, (b) Qxf and τ_f.

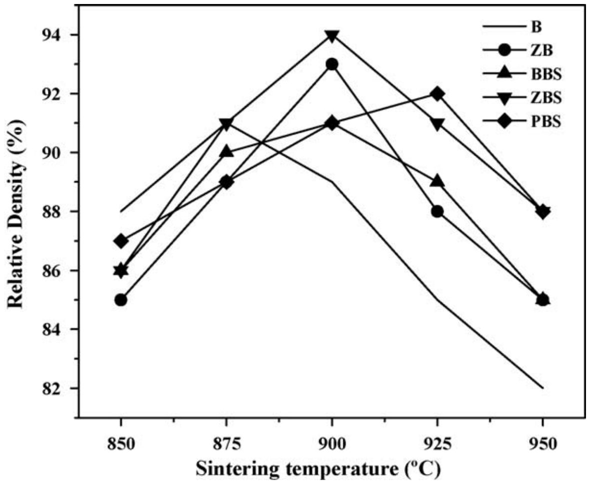

Fig. 5. Variation of relative density of 0.2 wt% of different glass fluxed $Ce_2(WO_4)_3$ ceramics.

Glasses such as B_2O_3 (B), $ZnO–B_2O_3$ (ZB), $BaO–B_2O_3–SiO_2$ (BBS), $ZnO–B_2O_3–SiO_2$ (ZBS) and $PbO–B_2O_3–SiO_2$ (PBS) are added to $Ce_2(WO_4)_3$ to lower the sintering temperature. Fig. 5 shows the variation of relative density with sintering temperature of 0.2 wt% different glass added $Ce_2(WO_4)_3$ ceramics. The theoretical density (D) of the glass added $Ce_2(WO_4)_3$ is calculated using the equation [1]:

$$D = \frac{W_1 + W_2}{(W_1/D_1) + (W_2/D_2)} \tag{2}$$

where W_1 and W_2 are the weight percentages of the $Ce_2(WO_4)_3$ and glass with densities D_1 and D_2, respectively. The densities of glasses are given in Table 1. The relative density of glass fluxed ceramic increases with sintering temperature, reaches a maximum and then decreases. Maximum densification of 94% is obtained for 0.2 wt% ZBS added $Ce_2(WO_4)_3$ ceramic at a sintering temperature of 900 °C. Maximum values of relative permittivity obtained for B, ZB, BBS and PBS added $Ce_2(WO_4)_3$ ceramics are 91, 93, 91 and 92%, respectively. The slight increase in relative density with the addition of 0.2 wt% glass addition could be attributed to liquid phase sintering, which promotes densification [16].

Fig. 6(a) and (b) shows the microstructures of 0.2 wt% ZB and ZBS glass fluxed $Ce_2(WO_4)_3$ ceramic sintered at 900 °C/4 h. The size of the $Ce_2(WO_4)_3$ grain decreased from 10–25 μm (see Fig. 3) to 0.2–1 μm with the addition of 0.2 wt% ZB and ZBS glass. This decrease in size of the grains is due to the lower sintering temperature [27].

The $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C/4 h has a relative permittivity of 12.4 with a quality factor of 10,500 GHz and temperature coefficient of resonant frequency, −39 ppm/°C. The ε_r and Qxf of 0.2 wt% different glass added $Ce_2(WO_4)_3$ ceramics are investigated by sintering at temperatures in the range 850–950 °C, and the results are shown in Fig. 7. The ε_r increases with sintering temperature reaches a maximum value and then decreases. The relationship between relative permittivity and sintering temperature shows the similar trend as the relationship between relative density and sintering

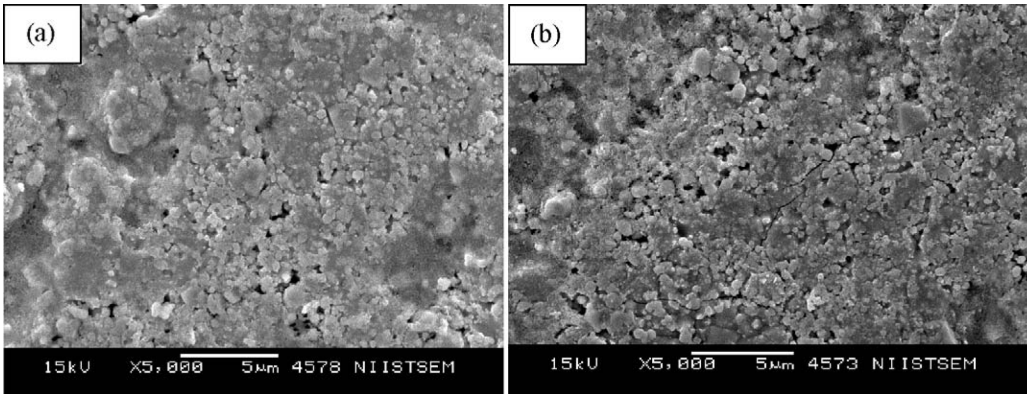

Fig. 6. SEM micrograph of 0.2 wt% (a) ZB and (b) ZBS glass fluxed $Ce_2(WO_4)_3$ ceramic sintered at 900 °C/4 h.

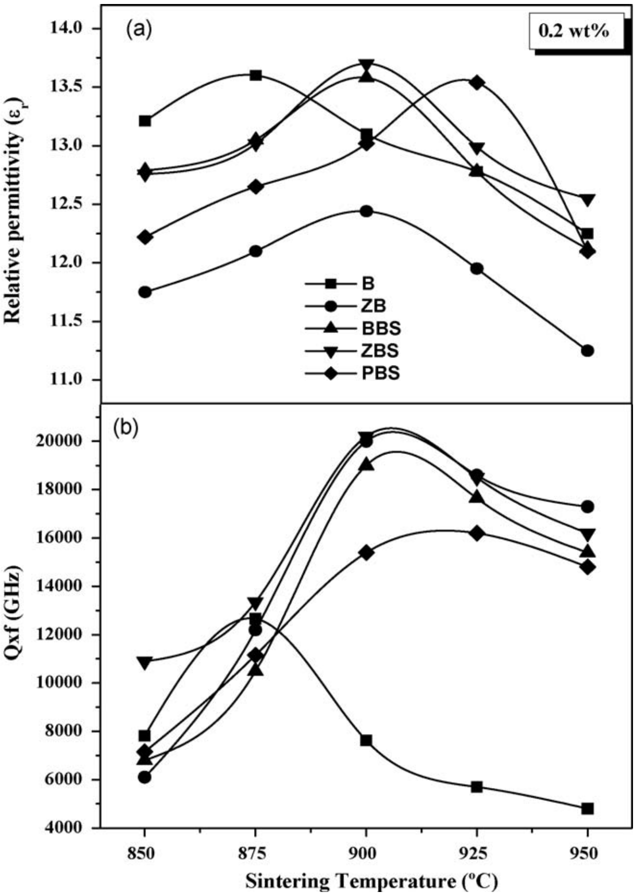

Fig. 7. Variation of (a) ε_r and (b) *Qxf* of 0.2 wt% glass fluxed $Ce_2(WO_4)_3$ ceramic.

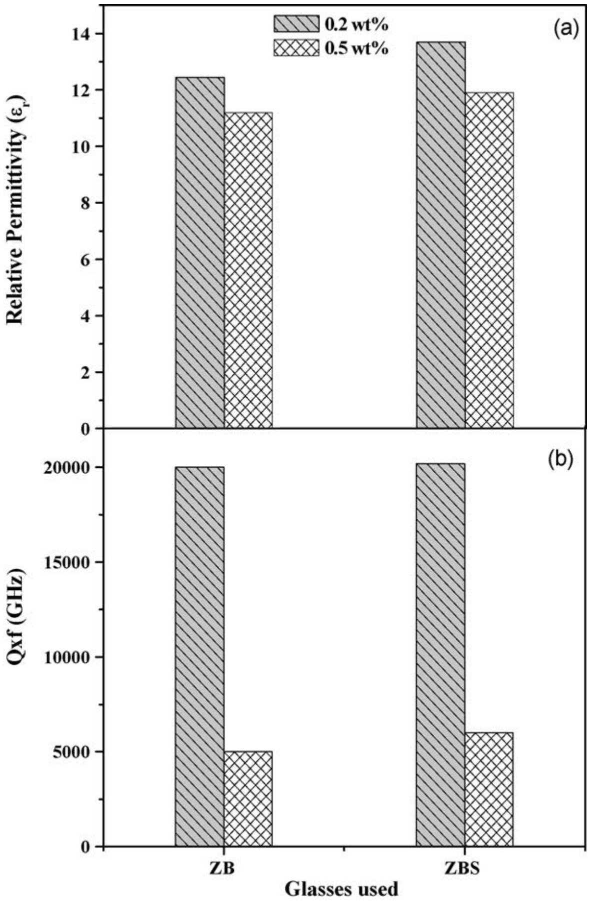

Fig. 8. Variation of (a) ε_r and (b) *Qxf* of 0.2 and 0.5 wt% ZB and ZBS glass fluxed $Ce_2(WO_4)_3$ ceramic.

temperature. Maximum ε_r of 13.6, 12.4, 13.5, 13.7 and 13.5 is obtained for 0.2 wt% B, ZB, BBS, ZBS and PBS glass added $Ce_2(WO_4)_3$ ceramic, respectively. The quality factor increases reaches a maximum and then decreases with sintering temperature for glass added $Ce_2(WO_4)_3$. The quality factor increased from 10,500 GHz for pure $Ce_2(WO_4)_3$ to 12,650, 20,000, 19,000, 20,200 and 16,200 GHz for 0.2 wt% B, ZB, BBS, ZBS and PBS doped $Ce_2(WO_4)_3$ ceramics, respectively (Fig. 8(b)). The best properties are obtained for 0.2 wt% ZB and ZBS fluxed with $Ce_2(WO_4)_3$ ceramic. Hence a detailed study on the microwave dielectric properties of different amounts of ZB and ZBS glass fluxed $Ce_2(WO_4)_3$ ceramic is carried out.

The variation of ε_r and *Qxf* with different wt% ZB and ZBS glass fluxed $Ce_2(WO_4)_3$ is shown in Fig. 8. The relative permittivity decreases from 12.4 to 11.2 when 0.5 wt% ZB glass is added and from 13.7 to 11.9 when 0.5 wt% ZBS is added to $Ce_2(WO_4)_3$ ceramic. The quality factor decreases with the addition of 0.5 wt% of ZB and ZBS glass in $Ce_2(WO_4)_3$ ceramic. Maximum quality factor of 20,200 GHz and relative permittivity 13.7 is obtained for 0.2 wt% ZBS glass fluxed $Ce_2(WO_4)_3$ ceramic sintered at 900 °C/4 h. The variation in τ_f with the addition of different wt% of glass added $Ce_2(WO_4)_3$ ceramics is shown in Fig. 9. In glass fluxed $Ce_2(WO_4)_3$ ceramics, τ_f is decreased with the addition of 0.2 wt% B, ZB and ZBS glass (τ_f of pure $Ce_2(WO_4)_3$ ceramic is −39 ppm/°C). The 0.5 wt% addition of ZB and ZBS glass to $Ce_2(WO_4)_3$ ceramic decrease the τ_f to −23 and −25 ppm/°C, respectively.

Most of the existing LTCC substrate materials having sintering temperature around 900 °C have very low quality factor. For e.g., $MgTiO_3–CaTiO_3 + ZnO–B_2O_3–SiO_2$ [28], $Ba_2Ti_9O_{20}$ + 50 vol% $BaO–B_2O_3–SiO_2$ [29], $ZnTiO_3 + V_2O_5$ [30] and $ZnNb_2O_6–TiO_2 + CaO–B_2O_3–SiO_2$ [31] have ε_r and

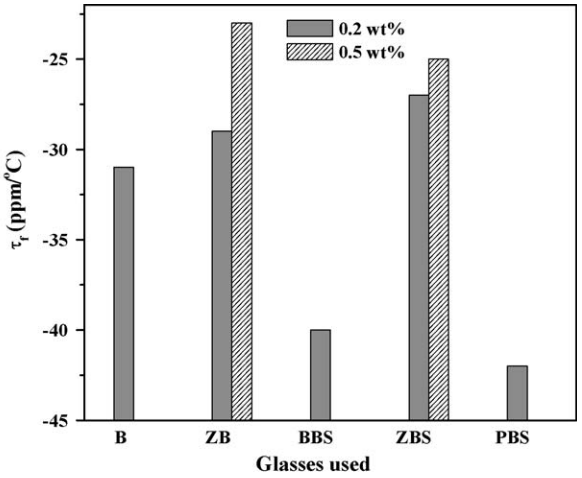

Fig. 9. Variation of τ_f with various glass fluxed $Ce_2(WO_4)_3$ ceramics.

Qxf of 9 and 7000 GHz, 13.2 and 1150 GHz, 20.6 and 8870 GHz and 19.2 and 11,000 GHz, respectively. $ZnTiO_3 + V_2O_5$ and $ZnNb_2O_6–TiO_2 + CaO–B_2O_3–SiO_2$ have relative permittivities of 20.6 and 19.2 which are slightly high for substrate applications. The reasonably good microwave dielectric properties of 0.2 wt% ZBS added $Ce_2(WO_4)_3$ show that it can be used as a possible candidate for LTCC substrate applications.

4. Conclusions

$Ce_2(WO_4)_3$ ceramic has been synthesized by the solid-state reaction method and the structure, microstructure and microwave dielectric properties are investigated. The $Ce_2(WO_4)_3$ ceramics have a poor sinterability. The optimized microwave dielectric properties of $Ce_2(WO_4)_3$ ceramic sintered at 1000 °C/4 h are $\varepsilon_r = 12.4$, $Qxf = 10{,}500$ GHz and $\tau_f = -39$ ppm/°C. Glasses such as B_2O_3, $ZnO–B_2O_3$, $BaO–B_2O_3–SiO_2$, $ZnO–B_2O_3–SiO_2$ and $PbO–B_2O_3–SiO_2$ have been added to lower the sintering temperature of $Ce_2(WO_4)_3$ ceramic. The effects of glasses on the sintering temperature, microstructure and microwave dielectric properties of $Ce_2(WO_4)_3$ are investigated. The $Ce_2(WO_4)_3 + 0.2$ wt% ZBS sintered at 900 °C/4 h has $\varepsilon_r = 13.7$, $Qxf = 20{,}200$ GHz and $\tau_f = -25$ ppm/°C.

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