This chapter reports for the first time the microwave dielectric properties of two new ceramics based on cerium - Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$. These two materials have been synthesized by conventional solid state ceramic route. The influence of glasses such as B$_2$O$_3$, ZnO-B$_2$O$_3$, BaO-B$_2$O$_3$-SiO$_2$, ZnO-B$_2$O$_3$-SiO$_2$ and PbO-B$_2$O$_3$-SiO$_2$ on the sintering temperature and microwave dielectric properties of Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics have also been investigated. Addition of small amount of glasses improved the properties of Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics. The results of this research established low temperature synthesis of Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics with improved microwave dielectric properties for dielectric substrate and possible Low Temperature Cofired Ceramic (LTCC) applications.
5.1 SYNTHESIS, CHARACTERIZATION AND MICROWAVE DIELECTRIC PROPERTIES OF TWO NOVEL DIELECTRIC CERAMICS

5.1.1 Introduction

The developments 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, have evolved in an unprecedented path for the last decade. An increasing effort has been directed towards attaining the miniaturization of components with the multilayer microwave integrated circuits (MIC), i.e., integration of passive components such as inductors, capacitors, resistors and line resonators into the substrate which carries the integrated circuits. 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 \( \varepsilon_r \) value, in order to minimize the cross-coupling effect with conductors, and a high quality factor (\( Q_{\omega_f} \)) value 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. Though extensive research has been made on single phase DR materials using cerium, very few reports has been made on its microwave dielectric properties. Hence we tried to prepare new single phase cerium compounds having good microwave dielectric properties and low sintering temperature that can be used for Dielectric Resonator and substrate applications.

Several researches on compound formation in rare earth tungstates have been reported. Mc Carthy et al. prepared and identified many compounds: \( \text{R}_2\text{O}_3/\text{WO}_3 = 3/1 \) (La-Lu, Y), 5/2 (Gd-Ho, Y), 7/4 (Nd-Lu, Y) and 1/1 (Nd-Lu, Y) etc. The system based upon \( \text{Ce}_2\text{O}_3 \) is difficult because of the instability of \( \text{Ce}_2\text{O}_3 \). Yoshimura et al. identified the stable phases in the system \( \text{Ce}_2\text{O}_3/\text{WO}_3 \). The subsolidus phase relation was also discussed for the ternary system \( \text{CeO}_2/\text{Ce}_2\text{O}_3/\text{WO}_3 \). Borchardt reported that \( \text{Ce}_2\text{O}_3.3\text{WO}_3 \) was only one compound which was produced by the reaction between \( \text{CeO}_2 \)
and WO$_3$ in air. The microwave dielectric properties of CeO$_2$-WO$_3$-TiO$_2$ ceramics have been reported in section 3.3 of Chapter 3 as $\varepsilon_r = 17$, $Q_{\mu \omega f} = 45550$ GHz in vacuum and $\varepsilon_f = 7$ ppm/$^\circ$C. The Ce$_2$(WO$_4$)$_3$ has a monoclinic crystal structure$^{12}$, though the microwave dielectric properties of the ceramic have not been reported to date.

A considerable amount of work has been done on the phase formation and structure of AO-V$_2$O$_5$ ($A$ = Ba, Mg, Zn) and Ce-V-O compounds.$^{14,15,16,17,18,19}$ Tsipis et al.$^{20}$ reported the stability and oxygen ion conductivity of zircon-type Ce$_{1-x}$A$_x$VO$_4$ ($A$ = Ca, Sr). A comparison between the Raman spectra of Ce$_{1-x}$Ca$_x$VO$_{4-0.5x}$ and Ce$_{1-x}$Bi$_x$VO$_4$ in which Ca$^{2+}$ and Bi$^{3+}$ are substituted for Ce$^{3+}$ in CeVO$_4$ has been reported by Hirata et al.$^{21}$ In the AO-V$_2$O$_5$ ($A$ = Ba, Mg, Zn) binary system, A$_3$(VO$_4$)$_2$ ($A$ = Ba, Mg, Zn) are low loss dielectric ceramic materials for microwave communication.$^{22,23,24}$ Chapter 4 discusses the microwave dielectric properties of BaO-CeO$_2$-TiO$_2$ system. Although considerable research has been done on BaO-V$_2$O$_5$ and CeO$_2$-V$_2$O$_5$ system, very little attention has been paid on the BaO-CeO$_2$-V$_2$O$_5$ system and its dielectric properties.

The present investigation reports for the first time two new dielectric ceramics based on cerium having low relative permittivity - Ba$_2$CeV$_3$O$_{11}$ and Ce$_2$(WO$_4$)$_3$.

### 5.1.2 Experimental

The Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics were prepared by the conventional solid-state ceramic route as described in Chapter 2, section 2.1.2. High purity chemicals CeO$_2$ (Treibacher, 99.9%), BaCO$_3$ (Aldrich, 99+%), V$_2$O$_5$ (Aldrich, 98+%) and WO$_3$ (Aldrich, 99+%) were used as the starting powders. Stoichiometric proportions of the chemicals were weighed and ball milled for 24 hours using zirconia balls in distilled water media. The slurry was dried and then calcined at 925°C/8h and 725°C/5h for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics respectively. The calcined powder was then ball milled for 24 hours. 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 minutes to expel the binder. The pellets were sintered
in air at temperatures in the range 950-1050°C and the dwell time was 4 hours. After sintering the samples were allowed to cool down to room temperature at the rate of 3°C/min. The samples were then polished to remove surface irregularities. The Ba$_3$V$_4$O$_{13}$ which formed as a secondary phase along with the Ba$_2$CeV$_3$O$_{11}$ ceramic was also prepared separately using the same method mentioned above at a calcination temperature of 625°C/5h and a sintering temperature of 700°C/4h.

The sintered samples were well polished and their bulk densities were found by Archimedes method. Structural phases were identified by powder X-Ray diffraction (XRD) technique using CuKα radiation. Scanning electron micrographs were recorded from the surface of sintered thermally etched samples to analyze the microstructure of the ceramics. The microwave dielectric properties were measured employing resonance method$^{25,26,27}$ as described in sections 2.4.2 to 2.4.5 of Chapter 2.

5.1.3 Results and Discussion

The synthesizing conditions such as calcination temperature, sintering temperature and their durations are optimized for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics to obtain the best density and dielectric properties. The samples are having good thermal and chemical stability as explained in section 3.3.4 of Chapter 3.

Figs. 5.1(a) and 5.2(a) show the variation of density with calcination temperature for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics respectively. The density increases and reaches a maximum at a calcination temperature of 925 and 725°C and then decreases for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics respectively. The variation of density with sintering temperature for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramic are shown in Figs. 5.1(b) and 5.2(b) respectively. The densities range from 4.88 to 5.89 g/cm$^3$ and 4.18 to 4.35 g/cm$^3$ for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramic respectively. Maximum density of 5.89 g/cm$^3$ (for Ce$_2$(WO$_4$)$_3$) and 4.35 g/cm$^3$ (for Ba$_2$CeV$_3$O$_{11}$) is obtained at a sintering temperature of 1000 and 1025°C respectively. The density decreased with further increase in sintering temperature. The maximum densification of 87% is obtained for
Ce₂(WO₄)₃ ceramics at a sintering temperature of 1000°C (theoretical density = 6.77 g/cm³).²⁸

**Fig. 5.1** Variation of bulk density of Ce₂(WO₄)₃ ceramic with (a) Calcination temperature and sintered at 1000°C for 4 hours (b) samples calcined at 925°C/8h and sintered at different temperatures for 4 hours

**Fig. 5.2** Variation of bulk density of Ba₃CeV₃O₁₁ ceramic with (a) Calcination temperature and sintered at 1025°C for 4 hours (b) samples calcined at 725°C/5h and sintered at different temperatures for 4 hours
5.1.3.1 Phase and Microstructural Analysis

Figs. 5.3 and 5.4 show the powder X-ray diffraction pattern of Ce₂(WO₄)₃ ceramic and Ba₂CeV₃O₁₁ ceramic sintered at 1000 and 1025°C for 4 hours respectively. The powder pattern of Ce₂(WO₄)₃ ceramic exhibits a single phase nature with monoclinic symmetry in agreement with ICDD file card numbers 31-0340. All peaks are indexed and the unit cell parameters are a = 7.828 Å, b = 11.730 Å and c = 11.600 Å. The XRD profile in Fig. 5.4 shows that Ba₂CeV₃O₁₁ ceramic is the main crystalline phase, in association with a second phase Ba₃V₄O₁₃ [ICDD File No. 36-1466]. The powder pattern of Ba₂CeV₃O₁₁ is compared with the JCPDS file No. 45-0093. Ba₃V₄O₁₃ has a space group 12/a with lattice parameters a = 15.07 Å, b = 8.941 Å and c = 10.16 Å.

SEM micrographs of Ce₂(WO₄)₃ and Ba₂CeV₃O₁₁ ceramic sintered at 1000 and 1025°C for 4 hours are shown in Figs. 5.5 and 5.6 respectively. The SEM studies on Ce₂(WO₄)₃ ceramic show that the densification is poor and the average grain size is about 10-25 μm. Small cracks are seen on the microstructure and this is the cause for poor densification in Ce₂(WO₄)₃ ceramic. Ba₂CeV₃O₁₁ ceramic sintered at 1025°C exhibits dense microstructure and has two types of grains which are identified as of
Fig. 5.5 SEM micrographs of \( \text{Ce}_2(\text{WO}_4)_3 \) ceramic sintered at 1000°C/4h

Fig. 5.6 SEM micrographs of \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) ceramic sintered 1025°C/4h

Fig. 5.7 EDXA spectrum of \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) ceramic sintered at 1025°C/4h

<table>
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<tr>
<td>Ba</td>
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<tr>
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<td>V</td>
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<td>V</td>
<td>48.44</td>
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Ba$_2$CeV$_3$O$_{11}$ and Ba$_3$V$_4$O$_{13}$. The average size of Ba$_2$CeV$_3$O$_{11}$ grain is about 10-25 $\mu$m. Small round shaped grains of size about 2 $\mu$m are of Ba$_3$V$_4$O$_{13}$. EDXA analysis of Ba$_2$CeV$_3$O$_{11}$ ceramic shown in Fig. 5.7 confirms the earlier XRD result on the presence of the secondary phase Ba$_3$V$_4$O$_{13}$.

5.1.3.2 Microwave Dielectric Properties

The variation of microwave dielectric properties of Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics with sintering temperature are shown in Figs. 5.8 and 5.9 respectively. The relative permittivity increases with sintering temperature up to a maximum of 10.8 (for Ce$_2$(WO$_4$)$_3$) and 14.9 (for Ba$_2$CeV$_3$O$_{11}$ ceramic) at 1000 and 1025°C respectively and decrease on sintering further at higher temperatures. The increase in relative permittivity is due to the increase in percentage density. The relationship between relative permittivity and sintering temperature show the same trend as that of density and sintering temperature (Figs. 5.8(a) and 5.9(a)). With increase in sintering temperature, $Q\nu xf$ increase, reach a maximum value and thereafter decrease for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics. The variation in $\varepsilon_r$ and $Q\nu xf$ is also consistent with that of density variation. The maximum $Q\nu xf$ of 10500 and 12700 GHz is obtained by sintering at 1000 and 1025°C for Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics respectively. At low sintering temperatures, the microwave quality factors are low due to the poor density and when the sintering temperature increase above 1025°C abnormal grain growth occur which degrade the quality factor (Figs. 5.8(b) and 5.9(b)). Inhomogeneous grain growth at high sintering temperatures increases the number of lattice imperfections and the dielectric loss increase. 29 The most important grain characteristics for microwave dielectric properties are the average grain size, the grain size distribution, the grain morphology and the grain orientation. Several studies revealed that the presence of a liquid phase, an increased concentration of structural defects, closed porosity etc. cause grain growth which in turn influence the dielectric properties. 30,31,32 The increase in sintering temperature from 740 to 820°C of Bi$_{12}$TiO$_{20}$ increases the mean grain size from $\approx$10 to $\approx$20 $\mu$m. 33 Penn et al. 30 reported that the dielectric loss of alumina is increased when the
grain size exceeds 3-4 μm. In alumina, when pure powder compacts are sintered, some grains grow extensively to enormous size with pores trapped within those large grains.\textsuperscript{34,35} Molla \textit{et al.}\textsuperscript{36} reported that moisture trapped in the pores increases the dielectric loss. The microstructures of the ceramic bodies proved that sintering at higher temperatures result in abnormal grain growth and corresponding microcracks occur in a polycrystalline ceramic. The internal stress and crack formation are responsible for the deterioration of dielectric properties when abnormal grain growth occurs.\textsuperscript{37}

Fig. 5.8 Variation of microwave dielectric properties of Ce\textsubscript{2}(WO\textsubscript{4})\textsubscript{3} ceramic sintered at 1000°C/4h (a) ε, (b) Q, and τf

Fig. 5.9 Variation of microwave dielectric properties of Ba\textsubscript{2}CeV\textsubscript{3}O\textsubscript{11} ceramic sintered at 1025°C/4h (a) ε, (b) Q, and τf

Fig. 5.8(b) and 5.9(b) shows the influence of the sintering temperature on the τf values of Ce\textsubscript{2}(WO\textsubscript{4})\textsubscript{3} and Ba\textsubscript{2}CeV\textsubscript{3}O\textsubscript{11} samples. The τf values ranged from -60 to -34 ppm/°C and -18 to -14 ppm/°C for the Ce\textsubscript{2}(WO\textsubscript{4})\textsubscript{3} and Ba\textsubscript{2}CeV\textsubscript{3}O\textsubscript{11} samples sintered in the temperature range of 900-1025°C and 950-1050°C respectively.
The $\text{Ba}_3\text{V}_4\text{O}_{13}$ which formed as a secondary phase along with $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramic has been separately prepared as a single phase material. The $\text{Ba}_3\text{V}_4\text{O}_{13}$ sintered at 700°C/4h has a percentage density of 94, relative permittivity ($\varepsilon_r$) = 12, quality factor ($Q_{\times f}$) = 22500 GHz and $\bar{\varepsilon}_f = -67$ ppm°C.

### 5.2 LOW TEMPERATURE SINTERING AND MICROWAVE DIELECTRIC PROPERTIES OF $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ AND $\text{Ce}_2(\text{WO}_4)_3$ CERAMICS

#### 5.2.1 Introduction

In LTCC technology, the dielectrics are needed to cofire with electrode metal such as silver, depending on the requirement of the small delay time of the signal and low power consumption. Most of the commercial low loss dielectric materials used for high-frequency applications show high quality factors and relative permittivities, but have a high sintering temperature above 1300°C. The commonly used two methods to reduce the sintering temperature of dielectric ceramics are addition of low melting glasses or low melting point materials and chemical processing. The first method has been commonly found effective to decrease the firing temperature in spite of slight degradation of microwave dielectric properties of ceramics. Intensive research is being carried out on liquid phase sintering using low loss glass additives because of the potential they offer and being the least expensive. The $\text{Ce}_2(\text{WO}_4)_3$ and $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramics synthesized has high sintering temperature of 1000 and 1025°C respectively and hence they cannot be cofired with silver electrode (melting point is 961°C) for LTCC applications. Hence their sintering temperatures need to be lowered for LTCC applications. This can be achieved by the addition of low melting and low loss glasses.

In this section we report the utilization of small levels of $\text{B}_2\text{O}_3$ and borosilicate glasses to the $\text{Ce}_2(\text{WO}_4)_3$ and $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramics in an attempt to prepare ceramics with a sintering temperature less than 950°C that could have potential applications as cofired circuit components.
5.2.2 Experimental

The Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics were prepared by the conventional solid-state ceramic route as described in section 5.1.2. The glass powders used in this investigation were B$_2$O$_3$ (abbreviated as B), ZnO-B$_2$O$_3$ (ZB), BaO-B$_2$O$_3$-SiO$_2$ (BBS), ZnO-B$_2$O$_3$-SiO$_2$ (ZBS) and PbO-B$_2$O$_3$-SiO$_2$ (PBS). For synthesizing glasses, high purity (Aldrich, 99.9 %) oxides/carbonates were weighed stoichiometrically and mixed for two hours in an agate mortar with pestle using distilled water as the medium. It was then melted in a platinum crucible above their deformation temperature (see Table 1.2 in Chapter 2), quenched and powdered. The calcined Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ powder is subsequently mixed with different weight percentages of various 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 temperatures in the range 850-1000°C in air for 4 hours. The bulk densities of the sintered samples were measured using Archimedes method. The structure of the samples were characterized using X-ray diffraction, microstructure using SEM, elemental analysis using EDXA and microwave characterization using resonance technique described in section 2.4.2 to 2.4.5 in Chapter 2.

5.2.3 Results and Discussion

5.2.3.1 Density and Microstructural Analysis

The samples are having good thermal and chemical stability as explained in section 3.3.4 of Chapter 3. Glasses such as B$_2$O$_3$ (B), ZnO-B$_2$O$_3$ (ZB), BaO-B$_2$O$_3$-SiO$_2$ (BBS), ZnO-B$_2$O$_3$-SiO$_2$ (ZBS) and PbO-B$_2$O$_3$-SiO$_2$ (PBS) are added to Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ to lower the sintering temperature. Figs. 5.10 and 5.11 show the variation of density with sintering temperature of 0.2 wt% different glass added Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ to lowered the sintering temperature. Figs. 5.10 and 5.11 show the variation of density with sintering temperature of 0.2 wt% different glass added Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ to lower the sintering temperature. The density of glass fluxed ceramic increases with sintering temperature, reaches a maximum and then decreases. For all glass doped Ba$_2$CeV$_3$O$_{11}$ ceramics, density is maximum at 975°C. Maximum density of 6.23 g/cm$^3$
(for Ce$_2$(WO$_4$)$_3$) and 4.58 g/cm$^3$ (for Ba$_2$CeV$_3$O$_{11}$) is obtained for 0.2 wt% PBS added Ba$_2$CeV$_3$O$_{11}$ ceramic at a sintering temperature of 925 and 975°C respectively. The high density obtained for PBS glass fluxed ceramic is due to the high density of PBS glass compared to other glasses used in the present study. Optimized densities of B, ZB, BBS and ZBS added Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics are 6.08 and 4.36, 5.91 and 4.39, 6.19 and 4.38, 5.90 and 4.37 g/cm$^3$ respectively. The slight increase in density with the addition of 0.2 wt% B, ZB, BBS, ZBS and PBS glass could be attributed to the liquid phase sintering, which promotes rapid densification.

![Fig. 5.10 Variation of density of 0.2 wt% of different glass fluxed Ce$_2$(WO$_4$)$_3$ ceramic](image1)

![Fig. 5.11 Variation of density of different wt% ZBS glass fluxed Ba$_2$CeV$_3$O$_{11}$ ceramic](image2)

Fig. 5.10 shows the comparison of densities of 0.2 and 0.5 wt% ZB and ZBS glass fluxed Ce$_2$(WO$_4$)$_3$ ceramic. The density is decreased from 5.88 to 5.81 g/cm$^3$ and 5.90 to 5.85 g/cm$^3$ with the addition of 0.5 wt% ZB and ZBS glass respectively. The variation of density with different wt% of ZBS glass added Ba$_2$CeV$_3$O$_{11}$ ceramic in the temperature range 800-1000°C is shown in Fig. 5.13. The decrease in bulk density at higher sintering temperature is probably due to the inhomogeneous evaporation of the liquid phase from grain boundaries causing incomplete wetting. Addition of 1 wt% ZBS glass to Ba$_2$CeV$_3$O$_{11}$ lowers the sintering temperature from 1025°C to 825°C. The addition of further amount of ZBS glass does not lower the sintering temperature. Maximum value...
of density \(4.46 \text{ g/cm}^3\) is obtained for 1 wt% ZBS glass added \(\text{Ba}_2\text{CeV}_3\text{O}_{11}\) ceramic sintered at \(825^\circ\text{C}\).

Fig. 5.12 Variation of density of 0.2 and 0.5 wt% ZB and ZBS glass fluxed \(\text{Ce}_2(\text{WO}_4)_3\) ceramic

Fig. 5.13 Variation of density of 0.2 wt% of different glass fluxed \(\text{Ba}_2\text{CeV}_3\text{O}_{11}\) ceramic

Fig. 5.14 Shrinkage curves of (a) \(\text{Ce}_2(\text{WO}_4)_3\) ceramic doped with 0.2 wt% ZBS glass and (b) \(\text{Ba}_2\text{CeV}_3\text{O}_{11}\) ceramic doped with 1 wt% ZBS glass

Fig. 5.14 (a) and (b) shows the shrinkage curves of \(\text{Ce}_2(\text{WO}_4)_3\) ceramic doped with 0.2 wt% ZBS glass and \(\text{Ba}_2\text{CeV}_3\text{O}_{11} + 1\) wt% ZBS glass respectively. The onset of shrinkage occurs around 800 and 600°C respectively for \(\text{Ce}_2(\text{WO}_4)_3\) ceramic doped with 0.2 wt% ZBS glass and \(\text{Ba}_2\text{CeV}_3\text{O}_{11}\) doped 1 wt% ZBS glass respectively. The shrinkage is complete only beyond 925°C for both the samples. An 11% shrinkage at 925°C is
observed for both Ce$_2$(WO$_4$)$_3$ ceramic + 0.2 wt% ZBS glass and Ba$_2$CeV$_3$O$_{11}$ + 1 wt% ZBS glass added ceramic.

Fig. 5.15 SEM micrograph of 0.2 wt% (a) ZB and (b) ZBS glass fluxed Ce$_2$(WO$_4$)$_3$ ceramic sintered at 875°C/4h

Fig. 5.16 SEM micrograph of (a) 1 wt% and (b) 3 wt% ZBS glass fluxed Ba$_2$CeV$_3$O$_{11}$ ceramic sintered at 825°C/4h

Fig. 5.15 (a) and (b) shows the microstructures of 0.2 wt% ZB and ZBS glass fluxed Ce$_2$(WO$_4$)$_3$ ceramic sintered at 875°C/4h. The size of the Ce$_2$(WO$_4$)$_3$ grain decreased from 10-25 μm to 0.2-1 μm with the addition of 0.2 wt% ZB and ZBS glass (see Fig. 5.5). This decrease in size of the grain is due to the lower sintering temperature and also due to liquid phase sintering. SEM micrographs of 1 wt% and 3 wt% ZBS glass added Ba$_2$CeV$_3$O$_{11}$ is shown in Fig. 5.16(a) and (b). Addition of 1 wt% ZBS glass
to Ba$_2$CeV$_3$O$_{11}$ improved the sinterability of the ceramic. The presence of dense grains indicate the improvement in the sinterability due to liquid phase sintering in 1 wt% ZBS glass added Ba$_2$CeV$_3$O$_{11}$ ceramic. During sintering, low melting glass exists along the dielectric grains in liquid phase. The glass phase assists in the densification of the ceramic through liquid-phase sintering.$^{52,53}$ Addition of 3 wt% ZBS glass increases the porosity$^{54}$ which in turn decreases the density of the ceramic.

5.2.3.2 Microwave Dielectric Properties

The Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramic sintered at 1000 and 1025°C/4h has a relative permittivity of 10.8 and 14.9 with a quality factor of 10500 and 12700 GHz and temperature coefficient of resonant frequency, -39 and -14 ppm/°C respectively.

![Graphs showing variation of dielectric properties](image)

Fig. 5.17 Variation of (a) $\varepsilon_r$ and (b) $Q_{\omega f}$ of 0.2 wt% glass fluxed Ce$_2$(WO$_4$)$_3$ ceramic

Fig. 5.18 Variation of (a) $\varepsilon_r$ and (b) $Q_{\omega f}$ of 0.2 wt% glass fluxed Ba$_2$CeV$_3$O$_{11}$ ceramic

The $\varepsilon_r$ and $Q_{\omega f}$ of 0.2 wt% different glass added Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramic are investigated by sintering at temperatures in the range 850-1000°C, and the
results are shown in Figs. 5.17 and 5.18 respectively. 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 density and sintering temperature. Maximum ε_r of 11.9, 11.2, 12.0, 11.3 and 11.9 is obtained for 0.2 wt% B, ZB, BBS, ZBS and PBS glass added Ce_2(WO_4)_3 ceramic respectively. For 0.2 wt% B, ZB, BBS, ZBS and PBS glass added Ba_2CeV_3O_11 ceramic maximum ε_r obtained is 14.9, 14.9, 15.0, 15.0 and 15.2 respectively. The high ε_r of PBS glass added ceramic is due to the high ε_r of PBS glass.

The quality factor increases reaches a maximum and then decreases with sintering temperature for Ce_2(WO_4)_3 with all glasses. The quality factor increased from 10500 GHz for pure Ce_2(WO_4)_3 to 12650, 20000, 20150 and 16200 GHz for 0.2 wt% B, ZB, BBS, ZBS and PBS doped Ce_2(WO_4)_3 ceramics respectively (Fig. 5.17(b)). With the addition of 0.2 wt% of glasses to Ba_2CeV_3O_11 ceramic, the Q美感 is found to increase for ZB (13300 GHz) and ZBS (14100 GHz) (Fig. 5.18(b)). The quality factor is influenced by many factors including bulk density, grain boundary, secondary phases and other defects as well as anharmonic lattice vibrations. The best property is obtained for 0.2 wt% ZB and ZBS fluxed with Ce_2(WO_4)_3 and 0.2 wt% ZBS doped Ba_2CeV_3O_11 ceramic. Hence a detailed study on the microwave dielectric properties of different amount of ZB and ZBS glass fluxed Ce_2(WO_4)_3 and ZBS glass doped Ba_2CeV_3O_11 ceramic is carried out.

The variation of ε_r and Q美感 with different wt% ZB and ZBS glass fluxed Ce_2(WO_4)_3 and ZBS glass fluxed Ba_2CeV_3O_11 ceramic are respectively shown in Figs. 5.19 and 5.20. The relative permittivity decreases from 11.2 to 10.9 when 0.5 wt% ZB glass is added and from 11.3 to 10.5 when 0.5 wt% ZBS is added to Ce_2(WO_4)_3 ceramic. It is found that relative permittivity shows a close relation with bulk density for different amount of ZBS glass fluxed Ba_2CeV_3O_11 ceramic. The quality factor decreases with the addition of ZB and ZBS glass in Ce_2(WO_4)_3 ceramic. Maximum quality factor of 20200 GHz and relative permittivity 11.3 is obtained for 0.2 wt% ZBS glass fluxed Ce_2(WO_4)_3 ceramic sintered at 900°C/4h. Maximum value of density (4.46 g/cm³), relative
permittivity (15.1) and quality factor (20300 GHz) is obtained for 1 wt% ZBS glass doped Ba$_2$CeV$_3$O$_{11}$ ceramic sintered at 825°C. Addition of further amount of ZBS glass decreases the quality factor due to the increase in porosity and the fact that glass has a higher dielectric loss.$^{56}$

The variation in $\tau_f$ with the addition of different wt% of glass added Ce$_2$(WO$_4$)$_3$ and Ba$_2$CeV$_3$O$_{11}$ ceramics are shown in Figs. 5.21 and 5.22. In glass fluxed Ce$_2$(WO$_4$)$_3$ ceramics, $\tau_f$ is decreased with the addition of 0.2 wt% B, ZB and ZBS glass ($\tau_f$ of pure Ce$_2$(WO$_4$)$_3$ ceramic is -39 ppm/$^\circ$C). The 0.5 wt% addition of ZB and ZBS glass to Ce$_2$(WO$_4$)$_3$ ceramic decrease the $\tau_f$ to -23 and -25 ppm/$^\circ$C respectively. A decrease in $\tau_f$ from -21 to -12 ppm/$^\circ$C is observed for 0.2 wt % PBS added Ba$_2$CeV$_3$O$_{11}$ ceramic. The $\tau_f$ of Ba$_2$CeV$_3$O$_{11}$ ceramic increases and reaches -42 ppm/$^\circ$C for 3 wt% ZBS addition.
The reasonably good microwave dielectric properties of 0.2 wt% ZBS doped \( \text{Ce}_2(\text{WO}_4)_3 \) and 1 wt% ZBS glass added \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) show that they can be used as possible candidates for LTCC substrate applications.

### 5.3 CONCLUSIONS

- Two new microwave dielectric ceramics based on cerium - \( \text{Ce}_2(\text{WO}_4)_3 \) and \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) have been synthesized and their structure, microstructure and microwave dielectric properties are investigated.
- The \( \text{Ce}_2(\text{WO}_4)_3 \) sintered at 1000°C/4h has a relative permittivity of 10.8 with a quality factor of 10500 GHz and temperature coefficient of resonant frequency, -39 ppm/°C.
- It is difficult to obtain \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) as a single phase material. The XRD pattern, SEM micrograph and EDXA spectrum of \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) reveal that a second phase \( \text{Ba}_3\text{V}_4\text{O}_{13} \) is formed along with \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) ceramic.
- The \( \text{Ba}_2\text{CeV}_3\text{O}_{11} \) ceramic (contain a small amount of \( \text{Ba}_3\text{V}_4\text{O}_{13} \)) sintered at 1025°C/4h has a relative permittivity 14.9 with a quality factor of 12700 GHz and temperature coefficient of resonant frequency, -14 ppm/°C.
The $\text{Ba}_3\text{V}_4\text{O}_{13}$ which formed as a secondary phase along with $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramic has a percentage density of 94, relative permittivity 12, quality factor 22500 GHz and $\tau_f = -67$ ppm/°C at a sintering temperature of 700°C/4h.

Glasses such as $\text{B}_2\text{O}_3$, $\text{ZnO-B}_2\text{O}_3$, $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$, $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ are added to $\text{Ce}_2(\text{WO}_4)_3$ and $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramics to lower the sintering temperature.

The microwave dielectric properties of 0.2 wt% ZBS added $\text{Ce}_2(\text{WO}_4)_3$ ceramic and 1 wt% ZBS glass added $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramic sintered at 900 and 825°C are $\varepsilon_r = 11.3$ and 15.1, $Q\times\tau_f = 20200$ and 20300 GHz and $\tau_f = -27$ and -21 ppm/°C respectively.

The 0.2 wt% ZBS doped $\text{Ce}_2(\text{WO}_4)_3$ and 1 wt% ZBS glass added $\text{Ba}_2\text{CeV}_3\text{O}_{11}$ ceramic can be used as possible candidates for LTCC applications.

This Chapter discusses the synthesis, characterization and microwave dielectric properties of two new compounds based on cerium - $\text{Ce}_2(\text{WO}_4)_3$ and $\text{Ba}_2\text{CeV}_3\text{O}_{11}$. The next Chapter gives the influence of rare earth substitution in Ce site on the structure and microwave dielectric properties of cerium oxide.
5.4 REFERENCES


