Microwave dielectric properties of polycrystalline Ca$_{5}$B$_{2}$TiO$_{12}$ ($B = \text{Nb, Ta}$) ceramics have been tailored using different glass additives such as B$_{2}$O$_{3}$, SiO$_{2}$, B$_{2}$O$_{3}$-SiO$_{2}$, ZnO-B$_{2}$O$_{3}$, Al$_{2}$O$_{3}$-SiO$_{2}$, Al$_{2}$O$_{3}$-B$_{2}$O$_{3}$-SiO$_{2}$, BaO-B$_{2}$O$_{3}$-SiO$_{2}$, MgO-B$_{2}$O$_{3}$-SiO$_{2}$, ZnO-B$_{2}$O$_{3}$-SiO$_{2}$, PbO-B$_{2}$O$_{3}$-SiO$_{2}$, and 2MgO-Al$_{2}$O$_{3}$-5SiO$_{2}$. The intentions of the investigation were (a) to study the effect of glass fluxing on the structure and density of Ca$_{5}$B$_{2}$TiO$_{12}$ ($B = \text{Nb, Ta}$) ceramics (b) to explore the possibility of low temperature sintering and hence to reduce the cost of production of the dielectrics (c) to improve the microwave dielectric properties of Ca$_{5}$B$_{2}$TiO$_{12}$ ($B = \text{Nb, Ta}$) ceramics. The influence of the above mentioned glasses on the phase purity, structure, microstructure, densification, sintering temperature and microwave dielectric properties of Ca$_{5}$Nb$_{2}$TiO$_{12}$ and Ca$_{5}$Ta$_{2}$TiO$_{12}$ ceramics are discussed. The results of this research established low temperature synthesis of Ca$_{5}$B$_{2}$TiO$_{12}$ ($B = \text{Nb, Ta}$) ceramics with improved microwave dielectric properties for dielectric resonator and possible Low Temperature Co-fired Ceramics (LTCC) applications.
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4.1 INTRODUCTION

The rapid advance in wireless communication in the past decade was because of the revolutionary progress in the discovery and development of increasingly sophisticated materials. The use of these materials in the circuitry of wireless devices, microelectronic technology and in monolithic microwave integrated circuits (MMIC)\(^1,2\) have led to dramatic decrease in the size and weight of devices such as cellular phones in recent years. Non-integrated bulk ceramics designed to be working as dielectric resonators (DRs), resonating at the frequency of the carrier wave and their efficiency to allow miniaturization and improved performance of microwave circuits have been the subject for discussion in the previous chapters. The excellent performance of the circuit is mainly controlled by the properties like dielectric constant (\(\varepsilon_r\)), unloaded quality factor (\(Q_u\)) and temperature variation of resonant frequency (\(f_0\)) of the material used. These stringent requirements prevent the use of all available DRs for practical applications and keep the development of advanced materials for wireless communication\(^3,4\) as a challenging area of research. The active work now in this field is the search for new materials\(^5,6,7\) and tailoring the properties of existing materials by solid solution formation,\(^8,9\) doping\(^10,11\) etc. In producing miniaturized devices, ceramic multilayer structures with low sintering temperature are needed because they can be co-fired with high conductivity metals such as silver, copper and their alloys.\(^12\) In this point of view low temperature co-fired ceramics (LTCC) has gained much attention because of their design and functional benefits over conventional techniques. LTCC materials will contribute much to the integration of electronic materials.\(^13\) Commercially available dielectric resonator materials for microwave application show high \(Q_u\) and high \(\varepsilon_r\), but need to be sintered at high temperatures for longer duration to attain better densification and thereby improved performance.\(^14,15,16\)

Complex perovskite \([A(B^{1/3}, B'^{2/3})O_3]\) materials are an important structural base for dielectric resonator applications and have excellent properties at microwave frequencies as explained in Chapter 3, Section 3.1.3. Ba based complex perovskites like \(\text{Ba(Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3\) and \(\text{Ba(Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3\) are reported\(^17\) to have good dielectric properties from the application point of view. The microwave dielectric properties of calcium based
complex perovskites\textsuperscript{18,19,20} are also reported in literature. As explained in Section 3.3.1 –
3.3.2 of Chapter 3, Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} and Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} ceramics posses reasonably good
dielectric properties at microwave frequencies. Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} has $\varepsilon_r = 48$, $Q_u \times f > 26\,000$
GHz and $\tau_f = +40$ ppm/$^\circ$C when sintered at 1550$^\circ$C/4h. Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} has $\varepsilon_r = 38$, $Q_u \times f >$
33\,000 GHz at 5GHz and $\tau_f = +10$ ppm/$^\circ$C, when sintered at 1625$^\circ$C for 4 hours. Efforts
have been made to tailor the microwave dielectric properties of these ceramics by doping
and solid solution formation (See Chapters 3, 5 and 6). More recently, these materials
were found (See Chapters 7 and 8) to be suited for the bandwidth enhancement of DR
loaded microstrip patch antenna and for the fabrication of wide band dielectric resonator
antennas. However the relatively high sintering temperature of these ceramics put
constraint over their use for practical purposes. Further, the demands for mass production
of the resonators require reliable, reproducible and cost effective processing of ceramics.
Several methods are reported in literature to reduce the sintering temperature of low loss
dielectric materials such as by (i) chemical synthesis\textsuperscript{21,22,23} (ii) using raw materials with
smaller particle size\textsuperscript{24} and (iii) liquid phase sintering\textsuperscript{25} by the addition of glassy materials.
The complex procedures involved, high cost of the chemicals and poor microwave
dielectric properties precludes the use of chemical synthesis for the industrial production
of DRs.\textsuperscript{26} Recent researches suggest that the addition of glassy materials as sintering aids
are most effective and simple method available to reduce the sintering temperature.
Efforts have been made to lower the sintering temperature of low loss dielectric resonator
materials like (Zr, Sn)TiO\textsubscript{4}\textsuperscript{27}, Ba\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20}\textsuperscript{28,29,30}, BaTi\textsubscript{4}O\textsubscript{9}\textsuperscript{31,32,33}, (Mg\textsubscript{0.5}Ca\textsubscript{0.5})TiO\textsubscript{3}\textsuperscript{34,35,36},
BiNbO\textsubscript{4}\textsuperscript{37} and Ba(Mg\textsubscript{1/3}Ta\textsubscript{2/3})O\textsubscript{3}\textsuperscript{38,39,40} with glass fluxing. The microwave dielectric
properties of DRs were affected by the liquid phase sintering due to the development of
microstructure at low firing temperature or the reaction between the host material and
additives. However for most of the systems with higher amount of glass, the reduction of
sintering temperature is usually accompanied by an abrupt decrease of physical and
dielectric properties of the matrix material due to the formation of secondary phases.\textsuperscript{41}
Only in a few cases could the sintering temperature be reduced without degradation of
dielectric properties due to the enhancement of density or the elimination of oxygen
vacancies\textsuperscript{42} in the material.
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With this point of view we have carried out investigations on the liquid phase sintering effect of \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (\( B = \text{Nb}, \text{Ta} \)) ceramics using several glasses like \( \text{B}_2\text{O}_3 \) (abbreviated as \( B \)), \( \text{Si}_2\text{O}_3 \) (\( S \)), \( \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( BS \)), \( \text{ZnO} - \text{B}_2\text{O}_3 \) (\( \text{ZB} \)), \( \text{Al}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( \text{AS} \)), \( \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( \text{ABS} \)), \( \text{BaO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( \text{BBS} \)), \( \text{MgO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( \text{MBS} \)), \( \text{ZnO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( \text{ZBS} \)), \( \text{PbO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) (\( \text{PBS} \)), and \( 2\text{MgO} - \text{Al}_2\text{O}_3 - 5\text{Si}_2\text{O}_3 \) (\( \text{MAS} \)). The goal of the present study is to find out an ideal glass system which promotes the vitreous phase sintering without deteriorating the microwave dielectric properties of \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (\( B = \text{Nb}, \text{Ta} \)) ceramics. Effort has also been made to understand the effect of concentration of glass additives on the sintering temperature, density, structure and microstructure of the host materials.

4.2 EXPERIMENTAL

The glass powders used in this investigation were classified into three categories. (i) Primary glasses like \( \text{B}_2\text{O}_3 \), \( \text{Si}_2\text{O}_3 \) (ii) Binary glasses such as \( \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \), \( \text{ZnO} - \text{B}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) and (iii) Ternary glasses like \( \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \), \( \text{BaO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \), \( \text{MgO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \), \( \text{ZnO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \), \( \text{PbO} - \text{B}_2\text{O}_3 - \text{Si}_2\text{O}_3 \) and \( 2\text{MgO} - \text{Al}_2\text{O}_3 - 5\text{Si}_2\text{O}_3 \). Recently Surendran et al.\(^{40}\) reported the thermal characteristics and dielectric properties of these glasses. High purity (99.9 %) oxides or carbonates were used as the raw materials for the synthesis of glass powder. The oxides were weighed in their appropriate stoichiometric compositional molar ratios and mixed in an agate mortar for 2h in distilled water medium. It was then melted in a platinum crucible above their softening temperature\(^{40}\) quenched and made into fine powder form.

\( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (\( B = \text{Nb}, \text{Ta} \)) materials were prepared by conventional solid-state ceramic route as explained in Section 2.1.2 of Chapter 2. Different weight percentage of the glasses were added to \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (\( B = \text{Nb}, \text{Ta} \)) materials calcined at \( 1350^\circ\text{C}/4\text{h} \). The prepared glass additives were well mixed with the matrix in distilled water medium in an agate mortar. The green pellets were preheated at \( 800^\circ\text{C} \) for 1h to expel the binder and then fired in their optimum temperature in a high temperature furnace to get maximum densification and thereby best microwave dielectric properties. Very slow cooling (\( 75^\circ\text{C}/\text{h} \)) was given to the sintered samples to avoid the possibility of cracking due to
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rapid thermal variations. The sintered ceramic pucks were polished and their bulk density was measured using Archimedes method. The structure and phase purity was examined by powder X-Ray diffraction (XRD) method using CuKα radiation and the surface morphology was investigated using scanning electron microscopic techniques.

The dielectric properties \( \varepsilon_r, Q_v \) and \( \tau_r \) of the materials were measured in the microwave frequency range using resonance technique\(^{43, 44, 45} \) as described in Chapter 2, sections 2.3.2 to 2.3.5.

4.3 RESULTS AND DISCUSSION

4.3.1 Phase Analysis

As it is described in Section 3.3.2 of Chapter 3, \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (B = Nb, Ta) has orthorhombic symmetry with a cell volume involving multiple simple perovskite subcells. At low temperatures, the different \( B \)-site atoms may be fully or partially ordered in crystallographically inequivalent \( B \)-sites and at high temperatures there may be more extensive disorder of atoms among the possible sites due to the influence of entropy. However, prolonged heating at a temperature below the sintering temperature of \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (B = Nb, Ta) ceramics could not make any significant change in its structure, density or microwave dielectric properties. Hence it could be concluded that no such ordering was observed in these ceramics by annealing. XRD study was made on \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (B = Nb, Ta) ceramics fluxed with various glasses in different weight percentages (0 - 2 wt. %). Addition of all glasses up to 1wt. % form single phase \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (B = Nb, Ta) ceramics except for \( \text{B}_2\text{O}_3 \), \( \text{ZnO} - \text{B}_2\text{O}_3 \) and \( \text{ZnO} - \text{B}_2\text{O}_3 - \text{SiO}_2 \), which form traces of borate based secondary phases from 0.2wt % onwards. The strong intensity peaks in the XRD pattern of \( \text{Ca}_5\text{B}_2\text{TiO}_{12} \) (B = Nb, Ta) ceramics added with 0.1 wt. % \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3-\text{SiO}_2 \), \( \text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2 \), \( \text{MgO-B}_2\text{O}_3-\text{SiO}_2 \) and \( 2\text{MgO-Al}_2\text{O}_3-5\text{SiO}_2 \) were found to be shifted to the higher angle region, indicating a decrease in lattice parameters and a resultant reduction in cell volume (not shown here). In the case of 0 to 2 wt. % of \( \text{B}_2\text{O}_3 \), \( \text{B}_2\text{O}_3-\text{SiO}_2 \), \( \text{ZnO-B}_2\text{O}_3 \), \( \text{ZnO-B}_2\text{O}_3-\text{SiO}_2 \), \( \text{BaO-B}_2\text{O}_3-\text{SiO}_2 \) and \( \text{PbO-B}_2\text{O}_3-\text{SiO}_2 \) glass added ceramics, the intensity peaks of the XRD profile were shifted to

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the low angle region indicating an increase in $a$, $b$, $c$ values and a corresponding increase in unit cell volume.

**Fig. 4.1** XRD pattern of 2 wt % of various glass added Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics

- $B \rightarrow B_2O_3$, $S \rightarrow SiO_2$, $BS \rightarrow B_2O_3 - SiO_2$, $ZB \rightarrow ZnO - B_2O_3$, $AS \rightarrow Al_2O_3 - SiO_2$, $ABS \rightarrow Al_2O_3 - B_2O_3 - SiO_2$, $BBS \rightarrow BaO - B_2O_3 - SiO_2$, $MBS \rightarrow MgO - B_2O_3 - SiO_2$
- $ZBS \rightarrow ZnO - B_2O_3 - SiO_2$, $PBS \rightarrow PbO - B_2O_3 - SiO_2$ and $MAS \rightarrow 2MgO - Al_2O_3 - 3SiO_2$

(a $\rightarrow$ Ca$_2$B$_2$O$_6$, b $\rightarrow$ Ca$_2$SiO$_4$, b' $\rightarrow$ Ca$_2$Ti$_5$O$_{12}$, c $\rightarrow$ Ca$_2$B$_2$SiO$_7$, d $\rightarrow$ Zn$_3$B$_2$O$_{11}$, e $\rightarrow$ CaAl$_2$SiO$_6$, f $\rightarrow$ CaBa$_2$(B$_2$O$_4$), g $\rightarrow$ Ca$_2$MgSi$_2$O$_7$, g' $\rightarrow$ Mg$_2$B$_2$O$_6$)

- h $\rightarrow$ Ca$_3$B$_2$O$_7$, h' $\rightarrow$ Ca$_2$ZnSi$_2$O$_7$, i $\rightarrow$ CaAlB$_2$O$_7$, j $\rightarrow$ PbB$_2$O$_7$

- k $\rightarrow$ Ca$_2$SiO$_4$, k' $\rightarrow$ Ca$_3$MgAl$_4$O$_{10}$ additional phases respectively)
The XRD pattern recorded from Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics fluxed with 2 wt % of various glasses are shown in Fig. 4.1. Addition of 2 wt % B₂O₃ promotes the formation of Ca₃B₂O₆ (JCPDS File Card No. 26 - 347) and SiO₂ addition causes the appearance of Ca₂SiO₄ (JCPDS File Card No. 31 – 302). Intensity peaks corresponding to Ca₂B₂SiO₇ (JCPDS File Card No. 29 – 303), β - Zn₅B₄O₁₁ (JCPDS File Card No. 9 – 153) and CaAl₂Si₂O₈ were found in the XRD pattern of Ca₅B₂TiO₁₂ (B = Nb, Ta) ceramics when 2 wt % of binary glasses like B₂O₃ - SiO₂, ZnO - B₂O₃ and Al₂O₃ - SiO₂ were added respectively to the host materials. The addition of even 1 wt % each of tertiary glasses to Ca₅B₂TiO₁₂ (B = Nb, Ta) ceramics form additional phases as is evident in the XRD profile. This is because of the easier decomposition of the glasses at high temperatures to yield its components to react with the matrix. Impurity phases of CaBa₂(B₂O₆)₂ (JCPDS File Card No. 39 – 230) are seen with the addition of BaO - B₂O₃ - SiO₂ and peaks corresponding to Mg₃(BO₃)₂ (JCPDS File Card No. 33 – 858) and Ca₂MgSi₂O₇ (JCPDS File Card No. 43 – 1491) appeared with the doping of MgO-B₂O₃-SiO₂ glass to Ca₅Nb₂TiO₁₂ powders. Whereas secondary phases of Ba₂SiO₄ (JCPDS File Card No. 26 – 1403) were found with the addition of BaO - B₂O₃ - SiO₂ and peaks representing CaMgSiO₄ (JCPDS File Card No. 35 – 590) were detected when Ca₅Ta₂TiO₁₂ powders were fluxed with 2 wt % MgO - B₂O₃ - SiO₂ glasses. The addition of even a small percentage of ZnO-B₂O₃-SiO₂ will promote the formation of Ca₂B₂O₅ (JCPDS File Card No. 18 - 279) and Ca₂ZnSi₂O₇ (JCPDS File Card No. 35 – 745) and this may be detrimental to the density and microwave dielectric properties. Traces of CaAlB₃O₇ (JCPDS File Card No. 29 – 280) and PbB₄O₇ (JCPDS File Card No. 15 – 278) were appeared in the XRD pattern of Ca₅Nb₂TiO₁₂ ceramics fluxed with 2 wt % of Al₂O₃ - B₂O₃ - SiO₂ and PbO - B₂O₃ - SiO₂ glasses respectively. The density and microwave dielectric properties of 2 wt % of ZnO - B₂O₃ - SiO₂ and PbO - B₂O₃ - SiO₂ glass added calcium tantalum titanates were much deteriorated due to the presence of satellite phases like Ca₂ZnSi₂O₇ (JCPDS File Card No. 35 – 745) and PbB₄O₇ (JCPDS File Card No. 15 – 278) respectively. Sintering of Ca₅Ta₂TiO₁₂ (B= Nb, Ta) ceramics with 2 wt % Al₂O₃ – B₂O₃ – SiO₂ glass also forms traces of CaAlB₃O₇ (JCPDS File Card No. 29 - 280) as their niobium analogue as is evident from the XRD profile. 2MgO-Al₂O₃-5SiO₂ was found to
be the most effective fluxing agent in Ca$_5$Nb$_2$TiO$_{12}$ ceramics also form secondary phases when excess glass is added as is visible in the XRD profile. Peaks corresponding to Ca$_5$SiO$_4$ (JCPDS File Card No. 31 – 302) and formation of polyphases such as Ca$_3$MgAl$_4$O$_{10}$ (JCPDS File Card No. 17 – 737) were detected in the XRD pattern as shown in Fig. 4.1. The density and microwave dielectric properties of Ca$_5$Ta$_2$TiO$_{12}$ ceramics were also least affected by the addition of 2MgO - Al$_2$O$_3$ - 5SiO$_2$ glass addition. Traces of impurity peaks corresponding to Ca$_3$MgAl$_4$O$_{10}$ (JCPDS File Card No. 17 – 737) were found with 2 wt % addition of 2MgO - Al$_2$O$_3$ - 5SiO$_2$ glasses to the matrix Ca$_5$Ta$_2$TiO$_{12}$ ceramics. It is possible that at temperatures above 1250°C, the multicomponent glasses decomposed and these components may remain in the grain boundary or react with the matrix material to form glass based additional phases and were detected in the XRD profile. Significant reduction in mechanical strength and crystalline nature of Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics were observed with the addition of 2 wt % of various glasses and the same was supported by decrease in the relative intensity of XRD peaks. This effect was more prominent with boron oxide based glasses and also more satellite phases were detected with these glasses.

4.3.2 Sintering and Densification

It is observed that glass fluxing facilitates vitreous sintering by forming low melting phases and hence reduces the sintering temperature of the ceramics. The variation of sintering temperature with wt% of glasses in Ca$_5$B$_2$TiO$_{12}$ (B= Nb, Ta) ceramics is depicted in Fig. 4.2 and 4.3. It is established earlier$^{46}$ that boron based glasses are more effective in lowering the sintering temperature. This may be due to the low softening temperature of B$_2$O$_3$. It is evident from Fig. 4.2 and 4.3 that by the addition of 2 wt% B$_2$O$_3$, sintering temperature of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics decreased significantly. 2 wt% addition of 2MgO - Al$_2$O$_3$ - 5SiO$_2$ glass has lowered the sintering temperature even up to 1320°C in the case of niobates and to 1350°C for the tantalates. However higher weight percentage of glass addition is needed to lower the firing temperature of the ceramics up to 950°C for the immediate use of these materials for LTCC applications, but it may considerably deteriorate the dielectric properties.
In liquid phase sintering, grain to grain material transport will be enhanced only if the additive can wet the grain of the matrix material. In such cases the transient glassy phase formed at a lower temperature can wet the ceramic and hence reduce the viscosity and enhances pore elimination resulting in densification. On the other hand, if the glass is not soluble in the ceramic, the wetting effect will be poor. Fig. 4.4 and 4.5 indicate the
densification characteristics of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics doped with various glasses in different weight percentage.

Out of the two primary glasses added to Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics, 0.1 wt. % of SiO$_2$ enhanced the bulk density, while B$_2$O$_3$ addition continuously decreased the density of the ceramic. Slight increase in percentage density was observed with the
addition of small amount of Al₂O₃ - SiO₂, MgO - B₂O₃ - SiO₂, ZnO - B₂O₃ - SiO₂ and 2MgO - Al₂O₃ - SiO₂. The percentage experimental density of Ca₅B₂TiO₁₂ (B = Nb, Ta) ceramics was found to be adversely affected by the addition of 0 – 2 wt. % of B₂O₃, B₂O₃ - SiO₂, ZnO - B₂O₃ and PbO - B₂O₃ - SiO₂.

The addition of more than 0.5 wt. % of all glasses decreased the percentage density of Ca₅B₂TiO₁₂ (B = Nb, Ta) ceramics. The excess quantity of glass doping leaves out more amount of decomposed glassy components in the matrix material. The trapped porosity associated with grain growth, evaporation of glass component and chemical reaction between glass and matrix material to form traces of secondary phases are the reasons for reduction in density with higher concentration of glass addition. Good densification was found for Si, Al and Mg based glass additives. Dopants with smaller ionic radii than Ca²⁺ results in the decrease of unit cell volume and hence increase in density. However excess addition of the same glasses was detrimental to density and is attributed to the formation of glass based secondary phases like CaAl₂Si₂O₈ and Ca₃MgAl₄O₁₀.

4.3.3 Microstructural Analysis

Scanning electron micrographs of a few typical glass added Ca₅B₂TiO₁₂ (B = Nb, Ta) specimens are shown in Fig. 4.6. Pure Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics were sintered at 1550°C/4h and 1625°C/4h respectively and their surface morphology is shown in Chapter 3, section 3.3.2. The grains are relatively large in size up to 10μm and clearly separated grain boundaries were visible in the micrograph. By the addition of 0.1 wt. % of 2MgO - Al₂O₃ - 5SiO₂ in Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics, the number of voids decreased considerably as shown in Fig. 4.6(a) and 4.6(b) respectively. The microstructure of 2MgO - Al₂O₃ - 5SiO₂ glass added Ca₅B₂TiO₁₂ (B = Nb, Ta) sintered specimens show uniformly sized grains of average size less than 10μm. This improvement in densification is in good agreement with a previous report that, liquid phase sintering can produce smaller grains than that formed by solid state process. The grain growth rate also found to be decreased by glass addition. Hence it can be concluded that the effect of glass addition was demonstrated not only by the decrease of the
sintering temperature, but also by densification of Ca$_3$B$_2$TiO$_{12}$ ($B =$ Nb, Ta) ceramics. Fig. 4.6(c) gives the surface morphology of 1 wt. % MgO – B$_2$O$_3$ – SiO$_2$ added Ca$_3$Nb$_2$TiO$_{12}$ ceramics and 4.6(d) represents the SEM picture of 1 wt % Al$_2$O$_3$ – B$_2$O$_3$ – SiO$_2$ glass fluxed Ca$_3$Ta$_2$TiO$_{12}$ ceramics.

Fig. 4.6 SEM pictures of some typical glass added Ca$_3$B$_2$TiO$_{12}$ ($B =$ Nb, Ta) ceramics

(a) Ca$_3$Nb$_2$TiO$_{12}$ + 0.1 wt % 2MgO – Al$_2$O$_3$ – 5SiO$_2$
(b) Ca$_3$Ta$_2$TiO$_{12}$ + 0.1 wt % 2MgO – Al$_2$O$_3$ – 5SiO$_2$
(c) Ca$_3$Nb$_2$TiO$_{12}$ + 1 wt % MgO – B$_2$O$_3$ – SiO$_2$
(d) Ca$_3$Nb$_2$TiO$_{12}$ + 1 wt % Al$_2$O$_3$ – B$_2$O$_3$ – SiO$_2$
(e) Ca$_3$Nb$_2$TiO$_{12}$ + 2 wt % ZnO – B$_2$O$_3$
(f) Ca$_3$Ta$_2$TiO$_{12}$ + 2 wt % ZnO – B$_2$O$_3$
It is evident from the figures that, the glassy material coated the grains of the matrix and reacted with the host material to form a glass based low melting phase. It increases the porosity of the host material. Distinct cracks with the segregation of secondary phases can be seen in the SEM micrograph and the density falls to even less than 90% of its theoretical value. Microstructural examination of sintered Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics added with 2 wt. % ZnO – B$_2$O$_3$ glass shows a large extent of porosity as is evident from Fig. 4.6 (e) and 4.6(f) respectively. Addition of 2 wt. % ZnO – B$_2$O$_3$ to Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics causes the formation of porous melt of glass, which further reduces the density of the host materials. However no additional phases are visible in the scanning electron micrograph though it appeared in the XRD spectra for higher weight percentage addition of glasses.

4.3.4 Microwave dielectric Properties

The microwave dielectric properties of glass doped ceramics depend on their density and presence of secondary phases. Generally, the addition of excess glass dopants to a ceramic lowers the sintering temperature accompanied by significant deterioration in the microwave dielectric properties. This happens when the decomposed glass remains in the host material, or due to the formation of glass based secondary phases because of the chemical reaction between glass and matrix. But it is noteworthy that, small amount of glass addition increases the density and microwave dielectric properties of the host material, because the liquid forming composition enables better pore elimination by enhancing the material transport. Hence the sintering of ceramics with glass may or may not improve the microwave dielectric properties depending upon the mode of reaction executed in the matrix with glass.

4.3.4.1 Primary Glasses

The variation of microwave dielectric properties of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics with the addition of primary glasses like B$_2$O$_3$ and SiO$_2$ in different concentration (0 to 2 wt %) are depicted in Fig. 4.7 and 4.8 respectively. Pure Ca$_5$Nb$_2$TiO$_{12}$ has $\varepsilon_r = 48$, $Q_u x f > 26000$ GHZ and $\tau_f = +40$ ppm/°C when sintered at
1550°C/4h (See Section 3.3.2 of Chapter 3). It can be seen from the Fig. 4.7 that the addition of any amount of B₂O₃ to Ca₅Nb₂TiO₁₂ deteriorated the dielectric properties except the decrease in τᵢ.

On the other hand 0.1 wt % of SiO₂ doping increased the quality factor and dielectric constant with a slight reduction in τᵢ, which is desired. In this case the Qᵢ x f increased to
27500 GHz and \( \varepsilon_r \) increased to 49. Higher amount of SiO\(_2\) (> 0.1\%) deteriorated the quality factor and dielectric constant with considerable decrease in \( \tau_f \).

The microwave dielectric properties of pure Ca\(_5\)Ta\(_2\)TiO\(_{12}\) ceramics sintered at \( 1625^\circ\)C/4h are \( \varepsilon_r = 38, Q_u x f > 33000 \text{ GHz} \) and \( \tau_f = +10 \text{ ppm/°C} \) (See Section 3.3.2 of Chapter 3). With the addition of B\(_2\)O\(_3\) from 0 to 2 wt \%, the dielectric constant decreases from 38 to 23, \( \tau_f \) changes from 10 ppm/°C to -3 ppm/°C and \( Q_u x f \) reduces to 10000 GHz (See Fig. 4.8). It is quite interesting to note the zero crossing of temperature variation of resonant frequency of Ca\(_5\)Ta\(_2\)TiO\(_{12}\) ceramics with an addition of about 1.3 wt \% of B\(_2\)O\(_3\). The formation of secondary phases like Ca\(_3\)B\(_2\)O\(_6\) and poor densification are supposed to be the reason for poor dielectric properties with large amount of B\(_2\)O\(_3\) addition. The addition of 0.1 wt. \% SiO\(_2\) to Ca\(_5\)Ta\(_2\)TiO\(_{12}\) ceramics enhances its \( \varepsilon_r \) and quality factor. \( \varepsilon_r \) increases to 39 and \( Q_u x f \) reaches 35000 GHz for 0.1 wt. \% addition of silica. Higher weight percentage addition of SiO\(_2\) adversely affected the values of \( \varepsilon_r \) and \( Q_u \) but improved \( \tau_f \) of the matrix material.

### 4.3.4.2 Binary Glasses

The microwave dielectric properties of binary glass added Ca\(_5\)Nb\(_2\)TiO\(_{12}\) ceramics are plotted in Fig. 4.9 as a function of weight percentage of glass. The doping of 0.2 wt. \% A\(_2\)O\(_3\) - SiO\(_2\) glass to the host Ca\(_5\)Nb\(_2\)TiO\(_{12}\) ceramics increased its \( Q_u \) and \( \varepsilon_r \) values by 12 and 3 percentages respectively. Above 0.2 wt. \% of A\(_2\)O\(_3\) - SiO\(_2\) addition a gradual decrease in dielectric properties of Ca\(_5\)Nb\(_2\)TiO\(_{12}\) was observed. This can be attributed to the formation of CaAl\(_2\)Si\(_2\)O\(_8\) secondary phase. B\(_2\)O\(_3\) - SiO\(_2\) and ZnO - B\(_2\)O\(_3\) glass addition to Ca\(_5\)Nb\(_2\)TiO\(_{12}\) ceramics seriously deteriorated their quality factor and dielectric constant. It is obvious from Fig. 9 that, monotonous decrease in \( \tau_f \) was observed by the addition of all binary glasses we experimented. 2 wt. \% addition of A\(_2\)O\(_3\) - SiO\(_2\) to Ca\(_5\)Nb\(_2\)TiO\(_{12}\) gives \( \varepsilon_r = 42, Q_u x f > 17000 \text{ GHz} \) and \( \tau_f = +13 \text{ ppm/°C} \). Out of the three binary glasses investigated A\(_2\)O\(_3\) - SiO\(_2\) was found to be most effective for improving the microwave dielectric properties of Ca\(_5\)Nb\(_2\)TiO\(_{12}\) ceramics. Addition of 0.1 wt. \% of A\(_2\)O\(_3\) - SiO\(_2\) to Ca\(_5\)Ta\(_2\)TiO\(_{12}\) enhanced the \( \varepsilon_r \) and \( Q_u \) of the host material as is evident from Fig. 4.10. In this case \( \varepsilon_r = 39.5 \) and \( Q_u x f > 36000 \text{ GHz} \) and \( \tau_f = 9 \text{ ppm/°C} \). Further
addition of the same glass deteriorated $\varepsilon_r$ and $Q_v$ whereas the $\tau_f$ value reduced to 2 ppm/°C for 2 wt. % of $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ glass addition.

Fig. 4.9 Microwave dielectric properties of 0 – 2 weight % binary glass added Ca$_5$Nb$_2$TiO$_{12}$ ceramics

Fig. 4.10 Microwave dielectric properties of 0 – 2 weight % binary glass added Ca$_5$Ta$_2$TiO$_{12}$ ceramics

When Ca$_5$Ta$_2$TiO$_{12}$ ceramics were added with different wt. % of $\text{B}_2\text{O}_3$-$\text{SiO}_2$ glasses, monotonous decrease in dielectric properties were observed. The $\tau_f$ decreased from 10 to 2 ppm/°C, $\varepsilon_r$ varied from 38 to 27 and quality factor decreased to 13000 GHz.
from the initial value of 33000 GHz. The dielectric properties of ZnO-B2O3 added Ca3Ta2TiO12 ceramics showed a continuous deterioration with the weight percentage of glass added as shown in Fig. 4.10. In this case poor densification and hence the deterioration of microwave dielectric properties occurred due to the formation of β-Zn3B4O11 secondary phase. Out of the three binary glasses B₂O₃-SiO₂, ZnO-B₂O₃ and Al₂O₃-SiO₂ added with Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics, 0.2 wt % of Al₂O₃-SiO₂ addition could only improve the microwave properties of the dielectric materials.

### 4.3.4.2 Ternary Glasses

The best and most well known liquid phase sintering agents are oxides of boron and copper. But it is reported that multicomponent glasses are more effective than single component glasses to reduce sintering temperature and to enhance density and dielectric properties. This is due to the fact that multicomponent glasses with SiO₄ and BO₃ configurations joined to form (Si – O – B – O) linkages with continuous atomic structures, which will have high electrical resistance and low dielectric loss.

The effect of addition of ternary glasses such as Al₂O₃ – B₂O₃ – SiO₂, BaO – B₂O₃ – SiO₂, MgO – B₂O₃ – SiO₂, ZnO – B₂O₃ – SiO₂, PbO – B₂O₃ – SiO₂ and 2MgO – Al₂O₃ – 5SiO₂ on the microwave dielectric properties of Ca₅Nb₂TiO₁₂ ceramics are shown in Fig. 4.11. Marginal increase in quality factor was observed with 0.1 wt. % addition of 2MgO – Al₂O₃ – 5SiO₂ and MgO – B₂O₃ – SiO₂ glasses, whereas the same increase was observed with 0.2 wt. % addition of Al₂O₃ – B₂O₃ – SiO₂ glass. Higher weight percentage doping of these glasses decreased the quality factor of Ca₅Nb₂TiO₁₂ ceramics and is due to the formation of glass based secondary phase. The same trend was observed in the variation of dielectric constant when Ca₅Nb₂TiO₁₂ was fluxed with these glasses. Addition of up to 0.2 wt % of Al₂O₃ – B₂O₃ – SiO₂, MgO – B₂O₃ – SiO₂ and 2MgO – Al₂O₃ – 5SiO₂ increased εᵣ of the host material from 48 to 50 and Qᵤ x f from 26000 GHz to 30000 GHz. Liquid phase sintering of Ca₅Nb₂TiO₁₂ ceramics with ternary glasses like BaO – B₂O₃ – SiO₂, ZnO – B₂O₃ – SiO₂ and PbO – B₂O₃ – SiO₂ deteriorated the microwave dielectric properties for 0 to 2 wt % of glass concentration.
However it is interesting to note that 0.1 wt % addition of PbO – B₂O₃ – SiO₂ to Ca₃Nb₂TiO₁₂ made more than 4% increase in the dielectric constant. It may due to the formation of PbB₄O₇ second phase (even with 0.1 wt % addition of the glass) due to chemical reaction between decomposed lead based glass and the matrix. Higher wt % of all ternary glasses decreased the Qᵣ and εᵣ of Ca₃Nb₂TiO₁₂ ceramics, may be due to the
formation of additional phases. It is worth to note the variation of $\tau_f$ with wt % of ternary glasses added in $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ ceramics. The addition of $\text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$, $\text{MgO - B}_2\text{O}_3 - \text{SiO}_2$, $\text{ZnO - B}_2\text{O}_3 - \text{SiO}_2$ and $2\text{MgO - Al}_2\text{O}_3 - 5\text{SiO}_2$ decreased the $\tau_f$ of the host material. It is quite expected as most of the glass compositions have negative $\tau_f$ values. On the other hand $\text{BaO - B}_2\text{O}_3 - \text{SiO}_2$ and $\text{PbO - B}_2\text{O}_3 - \text{SiO}_2$ glass fluxing resulted in an increase in the $\tau_f$ of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ ceramics with the wt. % of glass added. A linear increase was observed in the case of $\text{BaO - B}_2\text{O}_3 - \text{SiO}_2$ addition, while $\text{PbO - B}_2\text{O}_3 - \text{SiO}_2$ fluxing showed an initial decrease (up to 0.2 wt. %) and a later increase for higher concentration of glass. Considerable increase in dielectric constant and quality factor was observed with 0.1 wt. % addition of $\text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$, $\text{MgO - B}_2\text{O}_3 - \text{SiO}_2$ and $2\text{MgO - Al}_2\text{O}_3 - 5\text{SiO}_2$ glass addition. Fluxing of $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ ceramics with 0.1 wt. % $2\text{MgO - Al}_2\text{O}_3 - 5\text{SiO}_2$ glass increased its $\varepsilon_r$ to 39, $Q_u x f$ to 40000 (at 5 GHz) and lowered the $\tau_f$ to 8 ppm/°C. The $\tau_f$ reached negative values with 2 wt. % addition of $\text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$, $\text{MgO - B}_2\text{O}_3 - \text{SiO}_2$ and $2\text{MgO - Al}_2\text{O}_3 - 5\text{SiO}_2$ glasses. The addition of different wt. % of $\text{BaO - B}_2\text{O}_3 - \text{SiO}_2$, $\text{ZnO - B}_2\text{O}_3 - \text{SiO}_2$ and $\text{PbO - B}_2\text{O}_3 - \text{SiO}_2$ glasses continuously deteriorated the microwave dielectric properties of $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ ceramics. In the case of $\text{BaO - B}_2\text{O}_3 - \text{SiO}_2$ glass fluxing $\tau_f$ of $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ ceramics showed an increase unlike other glasses which showed a decrease.

In low temperature sintering, the microwave dielectric properties depends on the density and secondary phases formed due to the reaction between decomposed glass component and host material. For small percentage of glass doping no secondary phase was detected (except for $\text{B}_2\text{O}_3$, $\text{ZnO - B}_2\text{O}_3$ and $\text{ZnO - B}_2\text{O}_3 - \text{SiO}_2$) and hence the dielectric properties of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics were largely depend on density. The variation of $\varepsilon_r$ and $Q_u$ showed the same trend as that observed with density. The detailed investigation held on the glass addition of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics revealed that, ternary glasses were more effective compared with primary and binary glasses to improve the dielectric properties. Decrease in $\tau_f$ of the host materials with concentration of glass was quite expected as most of the glasses were reported to have negative $\tau_f$. However the increase in $\tau_f$ of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics with $\text{BaO - B}_2\text{O}_3 - \text{SiO}_2$ glass addition is quite surprising since it is reported to have a
negative $\tau_f$. It is observed that borate glasses were more effective in lowering the sintering temperature of matrix materials while dielectric properties witnessed more improvement with silica based glasses. $\text{SiO}_2$, $\text{Al}_2\text{O}_3 - \text{SiO}_2$, $\text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$, $\text{MgO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ and $2\text{MgO} - \text{Al}_2\text{O}_3 - 5\text{SiO}_2$ enhanced the density and microwave dielectric properties of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics. Off these, small amount of (about 0.1 wt. %) alumina and silica based glasses were found to be best suited for the effective vitreous phase sintering in $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) dielectrics, because of the improved microwave dielectric properties with the addition of these glasses. A ceramic material can be co-fired with internal copper or silver electrode only if the temperature reaches below the melting point of the electrode material (961°C for Ag and 1083°C for Cu). 2 wt. % glass additions on $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics could lower its sintering temperature only down to about 1320°C. Hence addition of a large amount of glass to $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) is needed for LTCC applications, which will further deteriorate the microwave dielectric properties.

4.4 CONCLUSIONS

- Effect of glass addition on the structure, density and microwave dielectric properties of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics have been investigated.

- The structure of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics were unaffected by the addition of small amount of primary, binary and ternary glasses. However glass based additional phases appeared in the XRD patterns for higher concentration of all glasses.

- Glasses like $\text{B}_2\text{O}_3$, $\text{B}_2\text{O}_3 - \text{SiO}_2$, $\text{ZnO} - \text{B}_2\text{O}_3$, and $\text{ZnO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ deteriorate densification and microwave dielectric properties of $\text{Ca}_5\text{B}_2\text{TiO}_{12}$ ($B = \text{Nb, Ta}$) ceramics. Boron oxide based glasses were found to be more effective in lowering the sintering temperature. 2 wt. % additions of glasses lowered the firing temperature of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ ceramics even down to 1320°C from 1550°C whereas the sintering temperature of $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ was brought down to 1450°C from 1625°C.
Microstructural analysis showed that small amount of glass additives like SiO₂, Al₂O₃ – SiO₂, Al₂O₃ – B₂O₃ – SiO₂, MgO – B₂O₃ – SiO₂ and 2MgO – Al₂O₃ – 5SiO₂ improved vitreous phase sintering and uniform grain growth along with increased densification. Higher amount of glass fluxing resulted in the formation of porosity and hence significant reduction in density.

It was observed that small amount of SiO₂, MgO – B₂O₃ – SiO₂, Al₂O₃ – SiO₂ and Al₂O₃ – B₂O₃ – SiO₂ and 2MgO – Al₂O₃ – 5SiO₂ increased the density and improved the microwave dielectric properties of Ca₅B₂TiO₁₂ (B = Nb, Ta) ceramics. Ca₅B₂TiO₁₂ (B = Nb, Ta) ceramics mixed with small amount of Al₂O₃ and SiO₂ based glass compositions exhibited good microwave dielectric properties. The improvement of microwave dielectric properties were more pronounced with ternary glasses than that with primary and binary glasses.

Marginal increase of 2 % density, 14 % quality factor and 4 % dielectric constant was attained when Ca₅Nb₂TiO₁₂ ceramics was doped with small amount of SiO₂, Al₂O₃ – SiO₂, Al₂O₃ – B₂O₃ – SiO₂, MgO – B₂O₃ – SiO₂ and 2MgO – Al₂O₃ – 5SiO₂. 0.1 wt % 2MgO – Al₂O₃ – 5SiO₂ glass added Ca₅Nb₂TiO₁₂ ceramics sintered at 1520°C/4h has εᵣ = 50, Qₑ x f > 30000 GHz and τₑ = +38 ppm/°C.

0.1 wt % addition of Al₂O₃-SiO₂, MgO-B₂O₃-SiO₂ and 2MgO-Al₂O₃-5SiO₂ to Ca₅Ta₂TiO₁₂, produced an enhancement of 4 % in εᵣ and 22 % in Qₑ x f values.

Addition of B₂O₃, Al₂O₃–B₂O₃–SiO₂, MgO-B₂O₃-SiO₂ and 2MgO-Al₂O₃-5SiO₂ glasses to Ca₅Ta₂TiO₁₂ shifted the τₑ of the ceramics from positive to negative values forming temperature stable compositions. Alumina based glasses were more effective in improving the temperature variation of resonant frequency.

The effect of glass additives on the sintering temperature and microwave dielectric properties of Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics were investigated in this Chapter. The forthcoming Chapter describes the method of cationic substitutions to tailor the microwave dielectric properties of Ca(Ca₁₋₄Nb₂₋₄Ti₁₋₄)O₃ complex perovskites material.
4.5 REFERENCES


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