CHAPTER 3

Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ (B = Nb, Ta)
CERAMICS:
EFFECT OF DOPANTS ON THE
MICROWAVE
DIELECTRIC PROPERTIES

This chapter discusses in detail about the complex perovskite type dielectric resonator materials and the introduction of a novel system: Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) into this family. Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ have been prepared by conventional solid-state ceramic route. The structure and microstructure were studied by X-Ray diffraction and Scanning Electron Microscopic techniques. The dielectric properties of the materials were measured in the 3-5 GHz microwave frequency range. Linear variations of microwave dielectric properties were observed in Ca$_5$Nb$_{2-x}$Ta$_x$TiO$_{12}$ solid solution system. The effect of various amounts of di-, tri-, tetra-, penta- and hexavalent impurities on the structure, microstructure, density and microwave dielectric properties of Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) complex perovskites have been investigated. Structure of the parent materials remained unchanged while slight increase in density was observed with small amount of certain dopants. Improvement in dielectric constant, quality factor and temperature coefficient of resonant frequency was observed with the doping of small amounts of MgO, ZnO, NiO, CuO, Co$_2$O$_4$, Cr$_2$O$_3$, SnO$_2$ and Sb$_2$O$_5$. A correlation between the microwave dielectric properties of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ [B = Nb, Ta] ceramics and ionic radius of the dopant has been observed.
3.1 SIMPLE AND COMPLEX PEROVSKITES

3.1.1 Introduction

Among the vast majority of mixed metal oxides used in modern chemical industry, perovskite-type oxides remain prominent. The perovskite oxides have the general formula $ABO_3$ ($A$ cation is larger in size than $B$). Although most of the numerous and interesting compounds with the perovskite structure are oxides, some carbides, nitrides, halides, and hydrides also crystallize in this structure. The first material reported in this family was CaTiO$_3$ later named as mineral perovskite by Gustav Rose in 1830's and named it after the memory of famous Russian mineralogist Count Lev Aleksevich von Perovski. The broad diversity of properties that these class of compounds exhibit is derived from the fact that around 90% of the metallic natural elements of the Periodic Table are known to be stable in a perovskite type oxide structure and also from the possibility of synthesizing multicomponent perovskites by partial substitution of cations in positions $A$ and $B$, giving rise to substituted compounds with formula of $A_{1-x}A'B_xB_1-xB'O_3$. These characteristics account for the large variety of reactions in which they are used as catalysts as well as applications in material science and electronics. Other important aspects of perovskites are related to the stability of mixed oxidation states or unusual oxidation states in the crystal structure.

3.1.2 $ABO_3$ Structure

![Fig. 3.1 (a) Ideal Perovskite ($ABO_3$) structure showing 6-fold coordination of $B$-site and 12-fold coordination of $A$-site cations (b) Unit cell of $ABO_3$ perovskite featuring the $A$-site enclosed by eight $BO_6$ octahedra](image)
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The ideal perovskite-type structure is cubic with space group $Pm\overline{3}m$. The unit cell formula of perovskite-type oxides is $ABO_3$, where $A$ is the larger and $B$ is the smaller cation. Fig. 3.1 (a) depicts the corner shared octahedra that form the skeleton of the structure, in which the centre position is occupied by the $A$ cation. In the unit cell, $A$ cations are located at position $[0, -\frac{1}{2}, -\frac{1}{2}]$, the $B$ at $[\frac{1}{4}, \frac{1}{4}, \frac{1}{4}]$ and three $O$ ions at $[0, \frac{1}{2}, \frac{1}{2}]$; $[\frac{1}{2}, 0, \frac{1}{2}]$; $[\frac{1}{2}, \frac{1}{2}, 0]$. Alternatively, this structure can be viewed with the $B$ cation placed at the center of the octahedron and the $A$ cation is at the center of the cube. The perovskite structure is thus a superstructure with an $REO_3$-type ($RE =$ Rare earth ions) framework built up by the incorporation of $A$ cations into the $BO_6$ octahedra. Hence in the $ABO_3$ structure, the $B$ cation is 6-fold coordinated and the $A$ cation is 12-fold coordinated with the oxygen anions. Besides the ionic radii requirements, another condition to be fulfilled for the stability of the structure is electroneutrality, i.e., the sum of charges of $A$ and $B$ equals the total charge of oxygen anions. This is attained by means of appropriate charge distribution of the form $A^{1+}B^{4+}O_3$ [eg. LiNbO$_3$], $A^{2+}B^{6+}O_3$ [eg. CaTiO$_3$], $A^{3+}B^{3+}O_3$ [eg. LaAlO$_3$] and $A^{6+}B^{6+}O_3$ [eg. REO$_3$] while $A^{4+}B^{2+}O_3$ is rare for cumblic reasons. In addition to this, partial substitution of $A$ and $B$ ions is allowed, thus yielding a plethora of compounds while preserving the perovskite structure. However, deficiencies of cations at the $A$- or $B$-sites or of oxygen anions are frequent, which results in defective perovskites. The nonstoichiometry in perovskites has been widely discussed in several reviews.

In the ideal structure, where the atoms are touching one another, the $B$-$O$ distance is equal to $a/\sqrt{2}$ ($a$ is the cubic unit cell parameter) while the $A$-$O$ distance is $a/2\sqrt{2}$ and the following relationship between the ionic radii holds: $R_A + R_O = \sqrt{2} (R_B + R_O)$. However, it was found that the cubic structure was still retained in $ABO_3$ compounds, even though this equation is not exactly obeyed. As a measure of the deviation from the ideal situation, Goldschmidt introduced a parameter named tolerance factor ($t$), defined by the equation:

$$t = \frac{R_O + R_A}{\sqrt{2} (R_O + R_B)}$$

(3.1)
which is applicable at room temperature to the empirical ionic radii. Although for an ideal perovskite \( t \) is unity, this structure is also found for lower \( t \)-values \((0.75 < t < 1.0)\). The ideal cubic perovskite structure appears in a few cases for \( t \)-values very close to unity at high temperatures. In most cases, different distortions of the perovskite structure appear. The naturally occurring compound CaTiO\(_3\) was originally thought to be cubic, but its true symmetry was later shown to be orthorhombic\(^7\) whereas SrTiO\(_3\) was found to be more symmetric with cubic structure and \( t = 1.0028 \). Deviations from the ideal structure with orthorhombic, rhombohedral, tetragonal, monoclinic, and triclinic symmetry are known, although the latter three ones are scarce and poorly characterized\(^9,10,11\). The distorted structure may exist at room temperature, but it transforms to the cubic structure at high temperature. This transition may occur in several steps through intermediate distorted phases. These deviations from the cubic perovskite structure may proceed from a simple distortion of the cubic unit cell, or an enlargement of the cubic unit cell, or a combination of both.

### 3.1.3 Complex perovskite structured compounds

Derivatives of simple perovskite structures are formed when either or both of the \( A \)- and \( B \)-site cations are replaced by combination of other cations located at specific crystallographic sites. Accordingly perovskites with general formula \( A(BB')O_3 \), \( (AA')BO_3 \) and \( (AA')(BB')O_3 \) are possible. In these types of compositions, change in temperature increases or decreases the amplitude of thermal vibrations and will not alter the positions of ions in their respective crystallographic positions and compositions is assumed to be in an ordered state. But there are some solid solutions in perovskite family, in which the random structure of cations exists only at elevated temperatures. If cations are ordered at only one site the compounds are commonly termed as double perovskite, whereas if ordering occurs at both sites they are referred to as complex or quadruple perovskites. Because of the potential to tolerate a wide range of elements of differing size and charge there exist a large number of permutations employing various cations in perovskite structure. Interestingly because of the industrial importance as dielectric resonators at microwave frequencies most of the perovskite compounds studied are not simple systems, but rather complex perovskite type with 1:1, 1:2 or 1:3 type of \( A \) and/or \( B \)-site ordering.
Ideal 1:1 ordered oxide perovskite comprises $A^{2+}B^{3+}B'^{4+}O_6$ (e.g. Sr$_2$DyRuO$_6$), $A'^{2+}B'^{4+}B^{4+}O_6$ (e.g. Ba$_2$CePtO$_6$), $A^{2+}B'^{2+}B'^{5+}O_6$ (e.g. Ba$_2$NiMoO$_6$), and $A^{2+}B'^{1+}B'^{7+}O_6$ (e.g. Ba$_2$NaReO$_6$) compositions with the occupancy of divalent cation in the $A$-site. When $A$ cation is trivalent two combinations of $B$-site cations are possible: $A'^{3+}B'^{2+}B'^{2+}O_6$ (e.g. La$_2$MgHfO$_6$) and $A'^{1+}B'^{2+}B'^{5+}O_6$ (La$_2$LiIrO$_6$). In a completely ordered 1:1 perovskite, the $B$ and $B'$ sublattices are occupied only by $B$ or $B'$ cations respectively and are ordered along [111]$_p$ planes or the vector $\frac{1}{2}[111]_p$. However for a completely random distribution (disorder) the sublattices can not be distinguished.

A genuine effort to make double perovskites with the general formula $A_3B^{2+}B'^{5+}O_9$ or $A(B'^{1+}B'^{2+}B'^{5+})O_9$ was first made by Rustam Roy\textsuperscript{12} based on complex perovskite compositions in Ba(B$_{1/2}$B'$_{1/3}$)$_3$O$_9$ and Ba(B$_{1/3}$B'$_{2/3}$)$_3$O$_9$. Later, Galasso \textit{et al.}\textsuperscript{13,14,15,16} studied the effect of substitution of different ions such as Ba, Sr, Ca and Pb on the $A$-site and Zn, Co, and Ni on the $B$ site in the $A_3B^{2+}B'^{5+}O_9$ complex perovskites using powder diffraction methods, where the $B'$-site was occupied by niobium or tantalum ions. It was observed\textsuperscript{15} that ideal 1:2 double perovskites are formed when the $B$-cations are ordered along [111]$_p$, or the vector $\frac{1}{3}[111]_p$ of the original cubic cell, and BO$_6$ and B'O$_6$ polyhedra are not tilted.

Perovskites which exhibit 1:3 ordering are relatively rare as most of the attempts to synthesize such compounds\textsuperscript{17,18} have resulted in ternary disordered perovskites. The 1:3 $A$-site ordered compounds have the general formula $AA'B_4O_{12}$ and include materials like CaCu$_3$Ge$_4$O$_{12}$\textsuperscript{19} and NdCu$_3$Ta$_4$O$_{12}$\textsuperscript{20}. The 1:3 $B$-site ordered compounds have the general formula $A_4BB'_3O_{12}$ like Ba$_4$LiSb$_3$O$_{12}$ compound reported\textsuperscript{17} by Alonso \textit{et al.} in 1987. It was observed that majority of ordered perovskites studied to date are oxide perovskites which exhibit 1:2 $B$-site ordering\textsuperscript{13}.

An unusual composition with the complex perovskite structure was reported by Cava \textit{et al.}\textsuperscript{21} in the Ca(Ca$_{1/4}$B$_{2/3}$Ti$_{1/4}$)O$_3$ (B = Nb, Ta) system, where mixing of three cations takes place in the $B$-site of the material. The material is actually a composition derived from CaTiO$_3$ - Ca$_2$B$_2$O$_9$ (B = Nb, Ta) polymorphs where the $B$-site of the latter was incorporated with Ti$^{4+}$ ions. High temperature phases of both Ca(Ca$_{1/4}$Nb$_{2/3}$Ti$_{1/4}$)O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/3}$Ti$_{1/4}$)O$_3$ ceramics were disordered, whereas low temperature phase of tantalum based material exhibited 1:2 type ordering and a mixing of 1:1 + 1:3 ordering for the
niobium analogue. Consequent to the complexity in ordering, the materials showed interesting variation in dielectric properties measured at 1 MHz.

3.2 **Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ (B = Nb, Ta) COMPLEX PEROVSKITES**

3.2.1 **Milestones in the research of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ (B = Nb, Ta) Ceramics**

Complex perovskite type titania and Nb/Ta based ceramics are of special interest as dielectric resonators for use in wireless communications. These materials exhibit a combination of high dielectric constant ($\varepsilon_r$) and low dielectric loss (high unloaded quality factor, $Q_u$). But they suffer from the drawback of relatively high temperature coefficient of resonant frequency ($\tau_f$), which is not preferable from the application point of view.

Investigations were made to tune the $\tau_f$ of these ceramics by solid solution formation between them. The CaTiO$_3$ - Ca$_4$Nb$_2$O$_9$ polymorphs has drawn much attention because of the opposite signs of $\tau_f$ for CaTiO$_3$ [$\varepsilon_r = 162$, $Q_u x f = 13000$ GHz and $\tau_f = + 859$ ppm/°C] and Ca$_4$Nb$_2$O$_9$ [$\varepsilon_r = 28$, $Q_u x f = 17000$ GHz and $\tau_f = - 22$ ppm/°C], which suggests the possibility of tuning $\tau_f$ to zero. The crystal structure of CaTiO$_3$ (the mineral perovskite) has been extensively studied and exists in several polymorphic forms which differ by a distortion of the framework of corner-connected [TiO$_6$] octahedra. The distortion originates from a large mismatch in the size of the A-type (Ca$^{2+}$) and B-type (Ti$^{4+}$) cations. Nevertheless, the room temperature phase is well established and belongs to orthorhombic symmetry with $Pnma$ space group. In contrast only limited information is available on the structure of Ca$_4$Nb$_2$O$_9$ ceramics, though the dielectric properties were reported by Kagata et al. In 1997, Hervieu et al. reported the existence of a high temperature orthorhombic and low temperature monoclinic structure for Ca$_4$Nb$_2$O$_9$. They proposed that both the Ca$_4$Nb$_2$O$_9$ polymorphs are derivatives of the perovskite structure with one fourth of the Ca ions occupying the B-site, when represented in Ca(Ca$_{1/3}$Nb$_{2/3}$)O$_3$ form. Recently Levin et al. made a detailed investigation about the octahedral tilting and cation ordering in Ca(Ca$_{1/3}$Nb$_{2/3}$)O$_3$ polymorphs. They suggested that four distinct perovskite related polymorphs exist in Ca(Ca$_{1/3}$Nb$_{2/3}$)O$_3$, which was identified with structures that combine octahedral tilting and different ordering of Ca/Nb ions in B-site. The polymorphs include two
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which has 1:2 ordering of Ca/Nb ions in the octahedral site.

Because of the interesting structural properties, recently Bendersky et al.\textsuperscript{35} studied the phase equilibria and microstructure of \( x \text{CaTiO}_3 - (1-x) \text{Ca}_4 \text{Nb}_2 \text{O}_9 \) ceramics and found that all the phases participating in equilibrium are solid solutions of the binary end members. Since both the end members have perovskite based structures, it is expected that the solid solution phases form as \( \text{Ca}_5 \text{Nb}_2 \text{TiO}_{12} \), which is a novel composition. For the sake of discussion, the material can be represented in the usual complex perovskite form as \( \text{Ca(Ca}_{1/4} \text{Nb}_{2/4} \text{Ti}_{1/4}) \text{O}_3 \), with \( A \)-site occupied by Ca and \( B \)-site by Ca, Nb and Ti in 1:2:1 proportion. Bendersky et al.\textsuperscript{35} suggested that the phase diagram of \( \text{Ca}_5 \text{Nb}_2 \text{TiO}_{12} \) has four single phase fields (i) cubic disordered \( (Pm\bar{3}m) \) (ii) a series of disordered \( \text{CaTiO}_3 \) – type polymorphs \( (Pnma) \) with different combinations of tilting (iii) a low temperature disordered/tilted \( (Pnma) \) phase and (iv) 1:1 or 1:2 ordered \( \text{Ca}_4 \text{Nb}_2 \text{O}_9 \) type fields. In addition a metastable transition to the 1:3 ordered phase occurs for a wide range of compositions. Most importantly they found that, the X-ray diffraction patterns of compositions in \( x \text{CaTiO}_3 - (1-x) \text{Ca}_4 \text{Nb}_2 \text{O}_9 \) with \( 0 < x < 1 \) were indexable by an orthorhombic lattice with parameters close to those of \( \text{CaTiO}_3 \). The same result was consolidated employing Transmission Electron Microscopic (TEM) techniques by observing different \([110]\) – type Selected Area Electron Diffraction (SAED) patterns, and also supported the \( Pnma \) symmetry.

Consequent to the invention of novel \( \text{Ca}_5 \text{Nb}_2 \text{TiO}_{12} \), in 1999, Cava et al.\textsuperscript{21} reported the 1 MHz dielectric properties of \( \text{Ca}_5 \text{Nb}_2 \text{TiO}_{12} \) and \( \text{Ca}_5 \text{Ta}_2 \text{TiO}_{12} \) materials. The authors studied the dielectric properties at different processing temperatures of the specimens and reported that in the vicinity of ambient temperature, the dielectric constants are approximately 35 and 23 for the Nb and Ta-based ceramics respectively, and dielectric losses of the order of 0.0002 and temperature variation of dielectric constant, \( \tau_\varepsilon < 5 \) ppm/°C. The distribution of Ca, Nb/Ta and Ti atoms on the \( B \)-site was often found to be dependent on temperature, as order-disorder transitions are expected due to the competition between size or charge driven ordering and the disorder induced by maximizing entropy. At low temperatures, for example, 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, Cava et al.\textsuperscript{21} observed a highly unusual behaviour of double zero crossing of $\tau_e$ with firing temperature. The samples fired at a temperature below 1450°C for both Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ showed negative $\tau_e$ values. Above this temperature, $\tau_e$ of both the ceramics shifted to positive values and the authors concluded that the positive $\tau_e$ state was due to the formation of an ordered state of the cations on the B-sites. This ordered state appears to be short-range in nature, since the conventional powder X-Ray diffraction patterns did not show the appearance of new diffraction peaks in the corresponding temperature interval. When the processing temperature was between 1500 and 1525°C for the niobate and between 1575 and 1600°C for the tantalate, the negative $\tau_e$ state returned. For both materials, this transition occurred abruptly and independent of firing time, suggesting the presence of a high temperature transition from an ordered B-site structure to a disordered B-site structure. Again, the conventional powder X-Ray diffraction patterns revealed that the materials remained single-phase perovskites and that there has been no long-range structural rearrangement or discontinuity in lattice parameter. Apparently the diffraction patterns only revealed a gradually decreasing unit-cell volume, with increasing firing temperature, and a continuously decreasing orthorhombic distortion.

Later Cava et al.\textsuperscript{36} explored the effect of chemical substitutions (Zr for Ti) in the niobium based compound that would enhance the kinetics of the formation of the short range ordered state and resulted in the low $\tau_e$ of Ca$_5$Nb$_2$TiO$_{12}$ ceramics. The low temperature coefficient state was at the borderline between ordered and disordered states of the Ca, Nb, and Ti ions in the B-sites of the perovskite lattice. The pure Zr analog of this phase, Ca$_5$Nb$_2$ZrO$_{12}$, had a positive $\tau_e$ value at all firing temperatures, as opposed to the generally encountered negative $\tau_e$ values for Ca$_5$Nb$_2$TiO$_{12}$. Hence intermediate compositions with low $\tau_e$ values were synthesized. However partial substitution of Zr for Ti were found to have a very significant effect on the $\tau_e$ values, suggesting that the added component had a strong effect on the order/disorder on the B-site sublattice, rather than having a simple mixing effect. However Zr substitutions at the higher concentrations significantly increased the range of firing temperature of the polycrystalline ceramics.
In 2001, a much more authoritative investigation on the dielectric properties and microstructure of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics were carried out by Bendersky et al. The authors applied transmission electron microscopy (TEM) techniques to probe into the details about the complex structural changes and dielectric behavior in Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ since X-ray powder diffraction method alone does not appear to be a good technique to approach the problem. It was found that different types of ordering between (111) planes, namely 1:1, 1:2 and 1:3, as well as distortions by tilting of octahedra, are involved in the formation of a microstructural state at an ambient temperature. Both the compounds in the as-sintered conditions have a microdomain structure but with a different type of ordering, 1:3 for Ca$_5$Nb$_2$TiO$_{12}$ and 1:2 for Ca$_5$Ta$_2$TiO$_{12}$. Moreover both the ceramics have a tilting phase transition from the disordered $Pm3m$ to distorted $Pnma$ (with the $a'b'a'$ tilt of octahedra) structures at temperatures that coincided with the observed second shift of $\varepsilon_r$ towards the negative values in the temperature versus $\varepsilon_r$ plot. The authors found that the structures of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics sintered at temperatures below 1450°C were different; the disordered $Pnma$ structure was found for Ca$_5$Ta$_2$TiO$_{12}$, and the 1:1 ordered $Pnma$ (monoclinic $P21/c=P121/n1$) structure was found for Ca$_5$Nb$_2$TiO$_{12}$. Because of kinetic reasons, the 1:1 ordering was only weakly developed during continuous cooling for Ca$_5$Nb$_2$TiO$_{12}$ sintered at temperatures above 1500°C. The dramatic changes in dielectric properties for materials sintered at temperatures above 1500°C are clearly associated with the formation of the twin structure for both materials. Comparison of the dielectric properties of the two compounds and their type of ordering led to the conclusion that 1:2 ordering of Ca$_5$Ta$_2$TiO$_{12}$ results in higher $\varepsilon_r$ and lower $\varepsilon_r$, as compared to the 1:1+1:3 ordering of Ca$_5$Nb$_2$TiO$_{12}$. Such an effect of ordering was recently demonstrated for the Ca(Ca$_{1/3}$Nb$_{2/3}$)O$_3$ polymorphs (having similar structure as that studied here) and the (Sr$_{1-x}$Ba$_x$)$_{1/3}$Ti$_{2/3}$O$_3$ system. The extreme chemical and microstructural complexity of the system, however, indicate that further analysis and characterization would be necessary to unambiguously associate the chemical and microstructural features with the dielectric properties, a correlation which has to date been made with very few members of this complex class of materials.
Investigations on the characterization of Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics at the microwave frequency range have not been tried though the materials were predicted as low loss at 1 MHz frequency. However, it is established that at microwave frequencies pore eliminated dense specimen devoid of secondary phases yields better results. Keeping this in mind the synthesizing conditions of Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics were optimized for maximum densification and hence better microwave dielectric properties.

3.3 SYNTHESIS, CHARACTERIZATION AND MICROWAVE DIELECTRIC PROPERTIES OF Ca(Ca₁/₄B₂/₄Ti₁/₄)O₃ (B = Nb, Ta) and Ca₅Nb₂₋ₓTaₓTiO₁₂ CERAMICS

3.3.1 Experimental

Ca(Ca₁/₄B₂/₄Ti₁/₄)O₃ (B = Nb, Ta) and Ca₅Nb₂₋ₓTaₓTiO₁₂ ceramics were prepared by conventional solid-state ceramic route as described in Chapter 2 Section 2.1. Stoichiometric amounts of high purity CaCO₃, TiO₂ (99.99+ %, Aldrich Chemical Company Inc., Milwaukee WI, USA), and Ta₂O₅/Nb₂O₅ (99.9+ %, Nuclear Fuel Complex, Hyderabad, India) were weighed and ball milled using zirconia balls in distilled water medium for 24 h. The mixture was dried and calcined. The calcinations were carried out at temperatures in the range 1200-1400°C for 4 h. The calcined powders were again ground well for 1 h in an agate mortar and then mixed with 5 wt % solution of poly vinyl alcohol (PVA) as the binder. The slurry was dried and ground again and pressed into cylindrical disks of diameter 14 mm and height about 7 mm under a pressure of 100 MPa. The green pellets were preheated at 600°C for 1 h to expel the binder and then sintered at high temperatures in air. Ca₅Nb₂TiO₁₂ samples were sintered in the temperature range 1500-1600°C and Ca₅Ta₂TiO₁₂ in the range 1575-1650°C (Nabertherm Furnace, Model LHT 02/18, Lilienthal, Germany). The effect of different sintering durations were also studied. 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. The sintered samples were thermally etched at a temperature about 50°C below the sintering temperature of each sample and the surface morphology was investigated using scanning
electron microscopic technique. The microwave dielectric properties such as dielectric constant, unloaded quality factor and temperature variation of resonant frequency was measured by using an HP 8510 C Network analyzer attached with a sweep oscillator and test parameter unit employing resonance method as explained in Section 2.3.2 to 2.3.5 of Chapter 2.

3.3.2 Results and Discussion

Fig. 3.1 shows the X-Ray diffraction patterns of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ powdered ceramics. The patterns are similar for both materials with a slight shift in the position of peaks. Both these materials are having orthorhombic symmetry.

![X-Ray diffraction patterns](image)

Fig. 3.1 X-Ray diffraction patterns of (a) Ca$_5$Nb$_2$TiO$_{12}$ and (b) Ca$_5$Ta$_2$TiO$_{12}$ ceramics

The lattice parameters for Ca$_5$Nb$_2$TiO$_{12}$ are $a = 5.510(4)\,\text{Å}$, $b = 7.907(9)\,\text{Å}$ and $c = 5.688(0)\,\text{Å}$. The theoretical density of Ca$_5$Nb$_2$TiO$_{12}$ is calculated to be 4.19g/cm$^3$. The Ca$_5$Ta$_2$TiO$_{12}$ has $a = 5.502(2)\,\text{Å}$, $b = 7.893(1)\,\text{Å}$ and $c = 5.668(5)\,\text{Å}$ with theoretical density 5.41g/cm$^3$. The tolerance factor ($t$) of $\text{ABO}_3$ structured ceramics are given by eqn. 3.1. In
the case of Ca$_3$B$_2$TiO$_{12}$ (B = Nb, Ta) perovskite materials, the equation can be modified with the inclusion of three cations in the complex perovskite as,

$$t = \frac{R_{Ca} + R_O}{\sqrt{2\{(R_{Ca}/4 + R_{Nb/Ta}/2 + R_O/4) + R_O\}}}$$  \hspace{1cm} (3.2)

where R denotes the radii of corresponding cations reported by Shannon. The value was found to be the same for both materials and is equal to 0.8823, which is much less than that for an ideal cubic structure ($t = 1$). It is established that the microwave dielectric properties of ceramic materials strongly depend on the synthesizing conditions.

Fig. 3.2 Variation of $\varepsilon_r$ and $Q_e$ of Ca$_3$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics with calcination temperature

Fig. 3.3 Variation of $\varepsilon_r$ and $Q_e$ of Ca$_3$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics with sintering temperature
With this view the calcination temperature, sintering temperature and their durations were optimized for \( \text{Ca}_5\text{Nb}_2\text{TiO}_{12} \) and \( \text{Ca}_5\text{Ta}_2\text{TiO}_{12} \) materials to get maximum density and best dielectric properties. The dependence of dielectric properties on the synthesizing conditions are depicted in the figures 3.2 to 3.4.

It is evident from Figs. 3.2 — 3.4 that the dielectric constant and quality factor increases with calcination and sintering temperature and with sintering duration up to a certain value of the latter and then decreased beyond the critical variable. The best density and dielectric properties of \( \text{Ca}_5\text{Nb}_2\text{TiO}_{12} \) ceramics are at a calcination temperature of 1350°C/4h and sintering temperature of 1550°C/4h. In the case of \( \text{Ca}_5\text{Ta}_2\text{TiO}_{12} \) ceramics the calcination temperature is the same as that of the niobates but the sintering temperature is 1625°C/4h. The maximum experimental density was obtained at optimum synthesizing conditions and the values were 4.06g/cm³ and 5.26g/cm³ for the niobates and tantalates respectively. In the optimized preparation conditions \( \text{Ca}_5\text{Nb}_2\text{TiO}_{12} \) has \( \varepsilon_r = 48, Q_u x f > 26000 \text{ GHz and } \tau_f = +40 \text{ ppm/°C}, \) whereas \( \text{Ca}_5\text{Ta}_2\text{TiO}_{12} \) has \( \varepsilon_r = 38, Q_u x f > 33000 \text{ GHz and } \tau_f = +10 \text{ ppm/°C} \).

It has been reported that in titanium based ceramics prolonged heating at a temperature slightly less than that of the sintering temperature will improve the density and dielectric properties. Hence we have annealed \( \text{Ca}_5\text{Nb}_2\text{TiO}_{12} \) samples at a temperature of 1350°C/10h and followed by annealing at 1150°C for 15 h each. Similarly \( \text{Ca}_5\text{Ta}_2\text{TiO}_{12} \) was annealed at 1450°C/10h and 1250°C for 15 h each. In both the cases for both materials no significant improvement in density or dielectric properties were observed. The density,
dielectric constant and $Q_e$ decreased on annealing while $\tau_f$ increased slightly. The sintered samples were kept in boiling water for 2 h. There was no change in density, dielectric properties or in XRD pattern indicating excellent chemical and thermal stability of the material. The sintered samples were thermally etched and the microstructures were examined under SEM. No secondary phases can be observed (Fig. 3.6). Uniformly distributed grains of relatively large size up to 10 $\mu$m can be seen in figure.

![Typical SEM photographs of (a) Ca$_3$Nb$_2$TiO$_{12}$ and (b) Ca$_5$Ta$_3$TiO$_{12}$ microwave ceramics](image)

**3.4 Ca$_{3}$Nb$_{2-x}$Ta$_x$TiO$_{12}$ [0 $\leq x \leq 2$] CERAMICS**

The Ca$_{3}$Nb$_{2-x}$Ta$_x$TiO$_{12}$ [0 $\leq x \leq 2$] ceramics show intermediate dielectric properties between the end members Ca$_3$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_3$TiO$_{12}$ as in the case of perfect solid-solutions$^{51}$. 

![Variation of density and $\varepsilon_r$ of Ca$_{3}$Nb$_{2-x}$Ta$_x$TiO$_{12}$ ceramics with $x$.](image) ![Variation of $\tau_f$ and $Q_e$ of Ca$_{3}$Nb$_{2-x}$Ta$_x$TiO$_{12}$ ceramics with $x$.](image)
CHAPTER 3

Since the ionic radii\textsuperscript{46} and charge are the same for both Nb and Ta ions the Ca$_5$Nb$_{2-x}$Ta$_x$TiO$_{12}$ forms a complete range of solid solution for all values of $x$ with properties changing linearly with $x$. The crystal symmetry was similar for all compositions with the orthorhombic structure like that of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$. Density and microwave dielectric properties are varying linearly between the title compounds for $x = 0$ to $x = 2$. Density increased with the amount of tantalum and can be attributed to the high molecular weight of Ta compared with Nb. Dielectric constant and $\tau_r$ was decreasing as $x$ increases and the unloaded quality factor was increasing with the value of $x$ (see Figs. 3.7 & 3.8). This variation can be attributed to the change in ionic polarizability\textsuperscript{52} and cell volume.

3.5 EFFECT OF DOPANTS IN Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ (B = Nb, Ta) CRERAMICS

3.5.1 Introduction

Commercially available dielectric resonator materials for microwave applications 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\textsuperscript{53,54,55}. As it has been outlined earlier in section 3.4 of this chapter, best microwave dielectric properties of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics were reported at a processing temperature of 1550°C and 1625°C respectively. The high sintering temperature of the ceramics also put constrain over their immediate use in practical applications. Several methods are proposed and investigated in literature, like (i) chemical synthesis\textsuperscript{56,57,58} (ii) using raw materials with smaller particle size\textsuperscript{59} and (iii) liquid phase sintering\textsuperscript{60} by the addition of glassy materials, to decrease the sintering temperature and improve the dielectric properties of low loss materials. However each technique has got many disadvantages which precludes the industrial production of high quality DRs.\textsuperscript{61} Doping of ceramics with suitable dopants\textsuperscript{62,63,64,65,66} have been established as an effective tool for tuning the properties of microwave dielectric materials. Hence to explore the possibility of bringing down the sintering temperature and improving the densification and microwave dielectric properties, aliovalent and isovalent dopants were added to calcined Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Nb$_2$TiO$_{12}$ powders. A comprehensive investigation was made to study
the effect of various dopants of different ionic radii and valency on the densification, sinterability and dielectric properties of Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics.

3.5.2 Experimental

The Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics were prepared through conventional mixed oxide route as described in Section 2.1.2 of Chapter 2. Stoichiometric amount of high purity CaCO$_3$, TiO$_2$ and Ta$_2$O$_5$/Nb$_2$O$_5$ were used as the starting materials. The powder mixture was ball milled in distilled water medium using zirconia balls in a plastic container for 24h. The slurry was dried and the reaction mixture thus obtained was calcined at 1350°C/4h and the resultant crispy material was ground into very fine powder. The calcined Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) precursor was divided into several batches and different mole % of dopants were added to selected weight of the parent material. The oxides to be doped were categorized based on their high temperature stable valency. Accordingly different mole % of various dopants such as divalent (MgO, MnCO$_3$, ZnO, NiO, CuO & Co$_3$O$_4$), trivalent (In$_2$O$_3$, Al$_2$O$_3$, Cr$_2$O$_3$, Y$_2$O$_3$, Bi$_2$O$_3$, Ga$_2$O$_3$ & Dy$_2$O$_3$), tetravalent (ZrO$_2$, SnO$_2$, HfO$_2$), pentavalent (Sb$_2$O$_3$, V$_2$O$_5$) and hexavalent (WO$_3$ & MoO$_3$) were added to calcined powders of the parent materials. The resultant mixture was well ground in distilled water medium, dried and mixed with 4 wt. % Poly Vinyl Alcohol (PVA) as binder, dried again and ground into very fine powder. Cylindrical ceramic pucks of 14 mm diameter and 6 - 7 mm height were formed under a uniaxial pressure of 100 MPa. Doped Ca$_5$Nb$_2$TiO$_{12}$ specimens were fired at an optimum temperature of 1550°C/4h, whereas the tantalates were sintered at 1625°C/4h. The sintered samples were well polished and their densities were measured by Archimedes methods. Phase purity of the materials was studied by powder X-Ray diffraction (XRD) analysis using CuK$\alpha$ radiation and microstructural analysis was done using scanning electron microscopic techniques. The dielectric properties $\varepsilon_r$, $\varepsilon$, and $\tan \delta$ of the materials were measured$^{42,43,44}$ in the microwave frequency range as described in Chapter 2, section 2.3.2 to 2.3.5.

It is to be noted that, dopants such as MnCO$_3$, Y$_2$O$_3$, Bi$_2$O$_3$, Ga$_2$O$_3$, Dy$_2$O$_3$, HfO$_2$, WO$_3$ & MoO$_3$ when added in 0 - 2 mole % to the parent Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) materials badly affected the densification and severely deteriorated their microwave dielectric
properties and hence the results are not described here. However the quality factor of \(\text{Ca}_5\text{B}_2\text{Ti}_2\text{O}_{12}\) (\(B = \text{Nb}, \text{Ta}\)) ceramics doped with 1 mole % of the above mentioned dopants are described in Fig. 3.22 to correlate ionic radius of the dopant with quality factor of the ceramics. We found a relationship between ionic radius of the dopant and average radius of the \(B\)-site ions in the parent complex perovskite material (discussed in a later section in this chapter) and only the dopants satisfying this condition were tried in different concentrations.

3.5.3 Results and Discussion

3.5.3.1 Phase Analysis

Pure \(\text{Ca}_5\text{Nb}_{2}\text{Ti}_2\text{O}_{12}\) and \(\text{Ca}_5\text{Ta}_{2}\text{Ti}_2\text{O}_{12}\) have an orthorhombic structure and belong to \(\text{Pnma}\) space group similar to \(\text{CaTiO}_3\) ceramics and the Bragg reflections were indexed accordingly. \(\text{Ca}_5\text{B}_2\text{Ti}_2\text{O}_{12}\) (\(B = \text{Nb}, \text{Ta}\)) ceramics doped with small (0 to 1 mole %) amount of all dopants form phase pure materials and hardly any additional phases appeared in the XRD spectrum. Moreover a slight shift of maximum intensity peaks towards the higher angle region was observed with di-and tetravalent dopants and shifted to the opposite direction with the doping of pentavalent impurities (figure not shown). It indicates a possible partial substitution of smaller divalent ions like \(\text{Mg}, \text{Zn}, \text{Ni}, \text{Cu}\) and \(\text{Co}\) for \(\text{Ca}^{2+}\), \(\text{Sn}\) and \(\text{Zr}\) for \(\text{Ti}^{4+}\) and \(\text{Sb}\) or \(\text{V}\) in place of \(\text{Nb}/\text{Ta}^{5+}\) in the complex perovskite \(B\)-site of the material. However, higher (> 1 mole %) amount of doping developed secondary phases in both the materials as is evident from Figs. 3.8(a) and 3.8(b). The additional phases formed, their scan angles in the XRD spectrum and ICDD file numbers are listed in Table 3.1.

3.5.3.2 Densification and Microstructural Analysis

Fig. 3.9 (a) and 3.10 (a) represents the variation of percentage densification of \(\text{Ca}(\text{Ca}_{1/4}\text{B}_{2/4}\text{Ti}_{1/4})\text{O}_3\) (\(B = \text{Nb}, \text{Ta}\)) dielectrics doped with divalent impurities such as \(\text{MgO}, \text{ZnO}, \text{NiO}, \text{CuO} & \text{Co}_2\text{O}_4\). The densification was relatively high with 1 mole % doping of \(\text{MgO}, \text{CuO} and \text{Co}_2\text{O}_4\). However these dopants in more than 1 mole % deteriorate the properties and lead to the formation of additional phases.
Fig. 3.8 XRD patterns of 2 mole % dopant added (a) Ca$_5$Nb$_2$TiO$_{12}$ and (b) Ca$_5$Ta$_2$TiO$_{12}$ ceramics (Italic letters denote the additional phases)
Table 3.1 Additional phases formed, their ICDD file numbers and positions when 2 mole % of various dopants were added to Ca(Ca$_{16}$B$_{24}$Ti$_{11}$)O$_3$ [B = Nb, Ta] ceramics

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Ca$_5$Nb$<em>2$TiO$</em>{12}$</th>
<th>Ca$_5$Ta$<em>2$TiO$</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Additional phases</td>
<td>Scan angle 28 (Degrees)</td>
</tr>
<tr>
<td>MgO</td>
<td>MgNb$<em>2$O$</em>{4.67}$</td>
<td>42.21</td>
</tr>
<tr>
<td>ZnO</td>
<td>ZnNb$<em>2$O$</em>{3.8}$</td>
<td>30.28</td>
</tr>
<tr>
<td>NiO</td>
<td>NiNb$<em>2$O$</em>{6}$</td>
<td>53.91</td>
</tr>
<tr>
<td>CuO</td>
<td>CaCuO$_2$</td>
<td>32.92, 43.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>Co$_2$Nb$<em>2$O$</em>{14}$</td>
<td>52.25</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>InNb$_2$O$_3$</td>
<td>29.87</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Ca$_3$Al$_2$O$_6$</td>
<td>33</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>CrNb$_2$O$_4$</td>
<td>53.57</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>CaSnO$_2$</td>
<td>17.38</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>CaZrO$_2$</td>
<td>43.09</td>
</tr>
<tr>
<td>Sb$_2$O$_3$</td>
<td>CaSb$_2$O$_6$</td>
<td>19.12</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>V$_2$Nb$<em>2$O$</em>{10}$</td>
<td>17.95, 43.93</td>
</tr>
</tbody>
</table>

Fig. 3.9 Percentage densification of 0 – 2 mole % (a) divalent and (b) trivalent dopant added Ca$_5$Nb$_2$TiO$_{12}$ ceramics

Fig. 3.10 Percentage densification of 0 – 2 mole % (a) divalent and (b) trivalent dopant added Ca$_5$Ta$_2$TiO$_{12}$ ceramics
Trivalent dopants like In$_2$O$_3$, Al$_2$O$_3$ and Cr$_2$O$_3$ have slightly improved the densities of Ca(Ca$_{14}$B$_{24}$Ti$_{14}$)O$_3$ (B = Nb, Ta) ceramics as seen in Fig. 3.9 (b) and 3.10 (b). It can be seen that the percentage densification is least for Al$_2$O$_3$ dopant, which is due to the poor sinterability of the ceramic. Similarly with tetravalent SnO$_2$ a densification of more than 98% was reached with 1 mole % of the dopant whereas with ZrO$_2$ a gradual decrease in the density was observed [See Figs. 3.11(a) and 3.12 (a)] and it was obviously due to poor sinterability of the ceramic owing to the very high sintering temperature of ZrO$_2$-based materials. In the case of 0.2 to 2 mole % of ZrO$_2$ doping, sintering temperature of the ceramics were increased by 50°C compared with that of the pure material to attain maximum density.
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The variation of percentage densification as a function of mole % of the pentavalent dopants (Sb$_2$O$_3$ and V$_2$O$_3$) are shown in Figs. 3.11 (b) and 3.12 (b). The percentage density of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ [B = Nb, Ta] ceramics reached about 98.5% with 1 mole % doping of Sb$_2$O$_3$. It was reported$^{68}$ that at high temperatures, Sb$_2$O$_3$ provides an ideal wetting medium for vitreous sintering to enhance densification. Recently Huang et al. reported$^{69}$ an increase in density and improved dielectric properties with V$_2$O$_3$ doping on Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ complex perovskites. But we found that doping of V$_2$O$_3$ in Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ [B = Nb, Ta] ceramics deteriorate the density and dielectric properties.

The surface morphology of pure Ca$_3$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ has described in Section 3.3.2 of this Chapter. Fig. 3.13 shows the microstructural evolution of two typical doped Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ (B = Nb, Ta) ceramic samples. It was found that the addition of 0.5 mole % of Cr$_2$O$_3$ into the Ca$_3$Nb$_2$TiO$_{12}$ material has resulted in better densification characteristics as seen from Fig. 3.13 (a). The grains were up to 5 µm in size. The surface micrograph presented a well packed grain structure with relatively smaller grains.

It is due to the dopant action to control the particle coarsening and thereby enhancing densification.$^{70}$ Fig. 3.13 (b) represents the surface morphology of Ca$_5$Ta$_2$TiO$_{12}$ samples doped with 2 mole % ZnO. Addition of ZnO promoted liquid phase sintering as they melt at a temperature much lower than 1625°C. But due to the insufficient wetting of the matrix, the densification remained poor in this case. More over the ZnO evaporation$^{71}$ has left out porosity between the grains which in turn lead to poor dielectric properties.

Fig. 3.13 SEM pictures of (a) 0.5 mole % Cr$_2$O$_3$ doped Ca$_3$Nb$_2$TiO$_{12}$ and (b) 2 mole % ZnO doped Ca$_5$Ta$_2$TiO$_{12}$ ceramics.

It is due to the dopant action to control the particle coarsening and thereby enhancing densification.$^{70}$ Fig. 3.13 (b) represents the surface morphology of Ca$_5$Ta$_2$TiO$_{12}$ samples doped with 2 mole % ZnO. Addition of ZnO promoted liquid phase sintering as they melt at a temperature much lower than 1625°C. But due to the insufficient wetting of the matrix, the densification remained poor in this case. More over the ZnO evaporation$^{71}$ has left out porosity between the grains which in turn lead to poor dielectric properties.

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3.5.3.3 Microwave Dielectric Properties

3.5.3.3.1 Divalent dopants

As described in Section 3.3.2 of this Chapter, Ca$_5$Nb$_2$TiO$_{12}$ has $\varepsilon_r = 48$, $Q_u \times f > 26000$ and $\tau_f = +40 \ \text{ppm/}^\circ \text{C}$, when sintered at 1550$^\circ$C/4h. The Ca$_5$Ta$_2$TiO$_{12}$ has $\varepsilon_r = 38$, $Q_u \times f > 33000$ and $\tau_f = +10 \ \text{ppm/}^\circ \text{C}$ at a sintering temperature of 1625$^\circ$C/4h. Fig. 3.14 & 3.15 shows microwave dielectric properties of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ complex perovskites doped with divalent dopants such as MgO, ZnO, NiO, CuO and Co$_3$O$_4$. In both the niobates and tantalate materials, $\varepsilon_r$ showed a gradual decrease with dopant concentration. It is known that ionic polarizability is the major factor contributing towards the $\varepsilon_r$ of the dielectric material. Accordingly ions with higher polarizability should have high $\varepsilon_r$. Ionic polarizabilities of the dopant cations Mg, Zn, Ni, Cu and Co are 1.32, 2.04, 1.23, 2.11 and 1.65 respectively and which is much less than that of divalent calcium (3.16). The possible substitution of divalent dopant for Ca$^{2+}$ will thus cause a resultant decrease in ionic polarizability and hence a reduction in $\varepsilon_r$.

The decrease in $\varepsilon_r$ with increased divalent concentration also supports the reduction in lattice parameter, cell volume and increased X-Ray density which may be due to the partial substitution of smaller dopant ions for bigger Ca$^{2+}$ ions. Variation of the temperature coefficient of resonant frequency in Ca$_5$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics as a function of mole percent of divalent dopants is depicted in Fig. 3.14 & 3.15. As is clear from the figures in both cases, $\tau_f$ decreased with increase in mole % of dopants except for CuO addition in which case it behaved in the reverse manner. It is interesting to note that in Ca$_5$Ta$_2$TiO$_{12}$ ceramics $\tau_f$ shows a zero value at $x = 1.6$ for Co$_3$O$_4$ and $x = 1.7$ for MgO addition. The variation of quality factor with mole % of divalent dopants in Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics are depicted in Figs. 3.14 and 3.15 respectively.

Consistent with the increased densification, 0.5 mole% MgO and CuO doped Ca$_5$Nb$_2$TiO$_{12}$ has a $Q_u \times f = 33000$ GHz and 30000 GHz, where as doping of 1 mole % each ZnO, NiO and Co$_3$O$_4$ increased the $Q_u \times f$ to 28000 GHz, 29000 GHz and 31000 GHz respectively. On the other hand the quality factor of Ca$_5$Ta$_2$TiO$_{12}$ reached a maximum of more than 40000 GHz and 38000 GHz with 0.5 mole % doping of MgO and CuO.
respectively. The doping of 1 mole % ZnO, NiO and Co$_3$O$_4$ increased the $Q \times f$ of Ca$_3$Ta$_2$TiO$_{12}$ ceramics to reach 39000 GHz, 38000 GHz and 38500 GHz respectively. Doping of more than 1 mole % divalent dopants was detrimental to the quality factor of Ca$_3$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics as they form additional phases. Out of the 5 divalent dopants investigated, MgO and Co$_3$O$_4$ were found to be more effective because they improved both $Q \times f$ and $\tau'_f$ of Ca$_3$B$_2$TiO$_{12}$ (B = Nb, Ta) ceramics.

**Fig. 3.14** Microwave dielectric properties of 0 – 2 mole % divalent dopant added Ca$_3$Nb$_2$TiO$_{12}$ ceramics

**Fig. 3.15** Microwave dielectric properties of 0 – 2 mole % divalent dopant added Ca$_3$Ta$_2$TiO$_{12}$ ceramic
3.5.3.3.2 Trivalent dopants

The microwave dielectric properties of Ca₅Nb₂TiO₁₂ and Ca₅Ta₂TiO₁₂ ceramics with dopants of oxidation state 3 are shown in Fig. 3.16 & 3.17. Doping with 1 mole % of In₂O₃ and Cr₂O₃ increased the $\varepsilon_r$ of Ca₅Nb₂TiO₁₂ by 2 %. In Ca₅Ta₂TiO₁₂ ceramics the same dopants in same quantity increased $\varepsilon_r$ from 38 to 39 (2.6 % increase). The quality factor of both the ceramics also showed the same trend as exhibited in $\varepsilon_r$.

![Fig. 3.16 Microwave dielectric properties of 0 - 2 mole % trivalent dopant added Ca₅Nb₂TiO₁₂ ceramics](Diagram1)

![Fig. 3.17 Microwave dielectric properties of 0 - 2 mole % trivalent dopant added Ca₅Ta₂TiO₁₂ ceramics](Diagram2)
The quality factor of Ca$_3$Nb$_2$TiO$_{12}$ ceramics reached as high as 34000 GHz (31\% increase) with 1 mole\% doping of Cr$_2$O$_3$ whereas with 1 mol\% In$_2$O$_3$, $Q_u f = 29000$ GHz and the same value was observed with 0.5\% Al$_2$O$_3$ doping. Ca$_3$Ta$_2$TiO$_{12}$ ceramics doped with 1 mole\% each of Cr$_2$O$_3$ and In$_2$O$_3$ has $Q_u f = 40500$ GHz and 37000 GHz respectively. 0.5 mole\% addition of Al$_2$O$_3$ could produce 10\% increase in the quality factor of Ca$_3$Nb$_2$TiO$_{12}$ and Ca$_3$Ta$_2$TiO$_{12}$ ceramics.

The increase observed in the value of $\varepsilon_r$ and $Q_u$ of both the ceramics can be attributed to the improvement in densification. With higher concentration of dopant ions, the measured dielectric constant and quality factor decreased which are due to high temperature phenomena like abnormal grain growth and formation of additional phases. The temperature coefficient of resonant frequencies of Ca$_3$Nb$_2$TiO$_{12}$ and Ca$_3$Ta$_2$TiO$_{12}$ ceramics as a function of mole\% of trivalent dopants is given in Figs. 3.16 and 3.17 respectively. Except for Al$_2$O$_3$, the $\tau_f$ of doped samples shifted towards the high positive values. Since Al$_2$O$_3$ being a negative $\tau_f$ dielectric resonator\textsuperscript{72} the fall in $\tau_f$ with this dopant was expected. In Ca$_3$Ta$_2$TiO$_{12}$ doping of 1.65 mole\% Al$_2$O$_3$ tune the $\tau_f \approx 0$ ppm/°C. It is evident that out of the three trivalent dopants studied, Cr$_2$O$_3$ increased $\varepsilon_r$ and $Q_u$ but deteriorated the $\tau_f$, whereas Al$_2$O$_3$ improved $\tau_f$ but with relatively less improvement in $\varepsilon_r$ and $Q_u$ of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ [B = Nb, Ta] ceramics.

### 3.5.3.3 Tetravalent dopants

Variation of microwave dielectric properties of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ [B = Nb, Ta] ceramics with the doping of different mole\% of tetravalent dopants (SnO$_2$ and ZrO$_2$) are shown in Figs. 3.18 and 3.19. $\varepsilon_r$ of both the ceramics increased with SnO$_2$ concentration for 0 to 1 mole\% and then decreased for higher percentage due to the formation of additional phases. The increase in $\varepsilon_r$ with Sn$^{4+}$ having lesser polarizability (2.83) than that of Ti$^{4+}$ (2.93) is contradictory to the relation between polarizability and $\varepsilon_r$. However it is believed that improvement in densification of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ ceramics with SnO$_2$ doping contribute more towards the $\varepsilon_r$ which hides the effect of small difference in polarizability\textsuperscript{56} between the two ions. An increase in $\varepsilon_r$ was expected with Zr$^{4+}$ of polarizability (3.25) which is higher than that of Ti$^{4+}$. However $\varepsilon_r$ of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_3$
and Ca(Ca$_{1/4}$Ta$_{1/4}$Ti$_{1/4}$)$_3$O$_7$ showed a linear decrease with increase in mole % of Zr$^{4+}$ doping and is assumed to be due to the poor sinterability and densification of the specimens. The investigations revealed that 1 mole % doping of SnO$_2$ in Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_7$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_7$ ceramics showed an improvement of 7 % in $Q_x f$ and which is due to increased densification of the samples. With ZrO$_2$ doping, poor densification of the ceramics lead to a linear decrease in the quality factor with increased dopant concentration.

![Fig. 3.18 Microwave dielectric properties of 0 – 2 mole % tetravalent dopant added Ca$_3$Nb$_2$TiO$_{12}$ ceramics](image1)

![Fig. 3.19 Microwave dielectric properties of 0 – 2 mole % tetravalent dopant added Ca$_3$Ta$_2$TiO$_{12}$ ceramics](image2)
The $\tau_r$ of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ specimens decreased from +40 to +33 ppm/°C and that of Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ decreased from +10 to +6 ppm/°C with the doping of 0 to 2 mole % SnO$_2$. This observation is consistent with a previous report of Matsumoto$^{73}$ in Ba(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_3$ ceramics. Doping of ZrO$_2$ on Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ specimens in 0 to 2 mole % yielded dielectric resonator materials with $\tau_r$ ranging from +40 to +24 ppm/°C, whereas with Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ the value varied from +10 to -2 ppm/°C. It is worthwhile to note that the doping of 1.6 mole % ZrO$_2$ in Ca$_5$Ta$_2$TiO$_{12}$ lead to temperature stable dielectric resonator. The modification of $\tau_r$in Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ [B = Nb, Ta] ceramics with doping of SnO$_2$ and ZrO$_2$ was believed to be due to the possible partial substitution of the dopant for tetravalent Ti$^{4+}$ ions.

3.5.3.4 Pentavalent dopants

The microwave dielectric properties of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ ceramics with 0 to 2 mole % pentavalent dopants (Sb$_2$O$_3$ and V$_2$O$_5$) are depicted in Fig. 3.20 and 3.21 respectively. It is evident from the figures that the doping of 0 to 1 mole % of Sb$_2$O$_3$ increased the $\varepsilon_r$ to reach a maximum of 49 for the niobates and 39 for the tantalate material and then decreased for 2 mole % of the dopant. The substitution of Sb$^{5+}$ with higher polarizability (4.27) than niobium (3.97) and increased density of the ceramic has contributed to the enhanced dielectric constant. On the other hand substitution of Sb$^{5+}$ with lesser polarizability than Ta$^{5+}$ (4.73), still increased the $\varepsilon_r$ of Sb$_2$O$_3$ doped Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ samples. Improved experimental density (more than 98%) of the specimens was assumed to be the reason behind this effect. The measured dielectric constant showed a decrease with increase in V$_2$O$_5$ concentration. This is due to the substitution of a less polarizable V$^{5+}$ ion (polarizability = 2.92) at the Nb/Ta site with higher polarizability. Moreover the percentage densification of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)$_3$O$_3$ ceramics with V$_2$O$_5$ doping was very poor which also reduced $\varepsilon_r$ of the samples. The quality factor of Ca$_5$Nb$_2$Ti$_3$O$_{12}$ and Ca$_5$Ta$_2$Ti$_3$O$_{12}$ ceramics showed 20 % and 14 % increase respectively with 1 mole % doping of Sb$_2$O$_3$ and the values decreased with 2 mole % of the dopant due to the existence of additional phases in the doped materials.
The quality factor of 0 to 2 mole % V$_2$O$_5$ doped ceramics showed an inverse relation with dopant concentration and is due to the poor sinterability and densification of the matrix with this dopant. The $\tau_f$ increased monotonously with increase in the V$_2$O$_5$ content in Ca$_3$Nb$_2$TiO$_12$ and Ca$_5$Ta$_2$TiO$_12$ ceramics. This coincides with a recent observation$^{62}$ that, temperature coefficient of resonant frequency increases with V$_2$O$_5$ doping. On the other hand $\tau_f$ of Sb$_2$O$_3$ doped Ca$_3$Nb$_2$TiO$_12$ and Ca$_5$Ta$_2$TiO$_12$ specimens decreases with mole % of the
dopant. Accordingly the $\tau_f$ of Ca$_5$Nb$_2$TiO$_{12}$ decreased from +40 to +33 ppm/°C and that of Ca$_5$Ta$_2$TiO$_{12}$ specimens varied from +10 to +5 ppm/°C.

Fig. 3.22 shows the variation of quality factor of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics doped with 1 mole % of different dopants as a function of ionic radii of the dopants. The average B-site ionic radius of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)O$_3$ are the same and is equal to 0.7213 Å. The ionic radius of the dopants at a coordination number of 6 is taken since the investigated dopants (di-, tri-, tetra- and pentavalent dopants can possibly get substituted in the B-site of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ [B = Nb, Ta] complex perovskites. In general when the ionic radii of the dopants are between 0.65 to 0.75 Å (i.e. close to the average ionic radii of the B-site ion in Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ [B = Nb, Ta] ceramics, the quality factor reached maximum values. However Mn$^{2+}$, Hf$^{4+}$ and Zr$^{4+}$ doping (0 to 2 mole %) has lowered the $Q_u x f$, even though ionic radius of the dopants were comparable to that of the average B-site ionic radius of the parent materials.

![Fig. 3.22 Plot of ionic radius of dopant versus quality factor of 1 mole % doped Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics.](image-url)
At the same time doping of Al$^{3+}$ and In$^{3+}$ improved the quality factor, though their ionic radius markedly deviate from the average B-site ionic radius of Ca(Ca$_{1/4}$B$_{1/4}$Ti$_{1/4}$)O$_3$ [B = Nb, Ta] ceramics. A similar observation was recently reported$^{65,74}$ in Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ and Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics and the $Q_v x f$ improved when the ionic radius of the dopant was close to the average B-site ionic radius of the complex perovskite material.

3.6 CONCLUSIONS

- Ca$_3$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics were prepared as single phase materials by conventional solid state ceramic route. The complex perovskite materials with an unusual occupancy of three cations in the B-site have orthorhombic symmetry and belong to Pnma space group. To the best of our knowledge these are the only dielectric resonator materials reported in literature with the mixing of three cations in the complex perovskite B-site.

- The synthesizing conditions of the ceramics were optimized and dielectric properties were measured in the microwave frequency range. Ca$_3$Nb$_2$TiO$_{12}$ has $\varepsilon_r = 48$, $Q_v x f > 26000$ GHz and $\tau_f = +40$ppm/°C, whereas Ca$_5$Ta$_2$TiO$_{12}$ has $\varepsilon_r = 38$, $Q_v x f > 33000$ GHz and $\tau_f = +10$ppm/°C. Annealing at lower temperatures could not make any improvement in the microwave dielectric properties of these complex perovskite materials.

- Solid solution phases in the Ca$_3$Nb$_{2-x}$Ta$_x$TiO$_{12}$ ($0 \leq x \leq 2$) system has been prepared and found that the density and dielectric properties shows a linear variation between that of the end members for all compositions.

- The effect of dopants on the structure, microstructure and microwave dielectric properties of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)O$_3$ dielectrics were investigated. Slight increase in density was found with the addition of MgO, ZnO, NiO, CuO, Co$_3$O$_4$, Cr$_2$O$_3$, In$_2$O$_3$, SnO$_2$ and Sb$_2$O$_3$. Divalent dopants in general, trivalent Cr$_2$O$_3$, In$_2$O$_3$ and pentavalent Sb$_2$O$_3$ were identified as the efficient candidates for improving the microwave dielectric properties of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)O$_3$ ceramics.
Increase in $\varepsilon_r$ and $Q_x$ of Ca(Ca$_{1/4}$B$_{2/4}$Ti$_{1/4}$)O$_3$ [$B = \text{Nb, Ta}$] dielectrics were attained with up to 1 mole % addition of these dopants. All the dopants mentioned above except CuO and Cr$_2$O$_3$ reduced the $\tau_f$ of both the parent materials. Temperature stable dielectric resonators were obtained with the addition of about 1.6 mole % each of MgO, Co$_3$O$_4$, Al$_2$O$_3$ and ZrO$_2$ to Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)O$_3$ material.

A correlation between the radius of the dopant ion and quality factor of the parent materials were established. It was found that dopants with ionic radii comparable to that of the average $B$-site radius of the perovskite structure became more efficient in improving the microwave dielectric properties of Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)O$_3$ ceramics.

In this Chapter we have introduced two novel microwave dielectrics in Ca(Ca$_{1/4}$Nb$_{2/4}$Ti$_{1/4}$)O$_3$ and Ca(Ca$_{1/4}$Ta$_{2/4}$Ti$_{1/4}$)O$_3$ compositions and described the effect of factors like synthesizing conditions, dopants etc. which controls the microwave dielectric properties of the ceramics. Next Chapter will throw light into the influence of glass additives on the sintering temperature and dielectric properties of the reported ceramics.
3.7 REFERENCES


Internet data, URL: [http://www.lsbu.ac.uk/dielectric-materials](http://www.lsbu.ac.uk/dielectric-materials)


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