Synthesis, Characterization and Properties of Ca$_5$A$_2$TiO$_{12}$ (A=Nb, Ta) Ceramic Dielectric Materials for Applications in Microwave Telecommunication Systems

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Abstract

Revolutionary progress in the field of microwave communication has lead to the invention of several dielectric resonator (DR) materials which are indispensable components in almost all modern telecommunication systems. High dielectric constant materials are very important in micro-electronic technologies such as dynamic random access memory (DRAM), substrates for microwave integrated circuits (MIC) and as gate dielectrics. Recently, Cava et al. reported the low-frequency (1 MHz) dielectric properties of the system Ca$_5$A$_2$TiO$_{12}$ (A=Nb, Ta). In the present paper, we report the microwave dielectric properties of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ ceramics for the first time. The effects of synthesising conditions, doping and annealing on the density and microwave dielectric properties of these ceramics are also investigated.

The ceramic resonators Ca$_5$A$_2$TiO$_{12}$ (A=Nb, Ta) were prepared by a conventional solid-state ceramic process. Stoichiometric amounts of high-purity CaCO$_3$, TiO$_2$, Nb$_2$O$_5$/Ta$_2$O$_5$ were weighed and ball milled using zirconia balls in distilled water medium for 24h. The mixture was dried and calcined at temperatures in the range 1200-1400°C for 4h each. The calcined powders were again well ground and pressed into cylindrical disks of diameter 14 mm and height about 7 mm under a pressure of 200 MPa. The green pellets were preheated at 600°C for 1h to expel the binder. Ca$_5$Nb$_2$TiO$_{12}$ samples were sintered in the temperature range 1500-1600°C and Ca$_5$Ta$_2$TiO$_{12}$ in the range 1575-1650°C. The effects of different sintering durations were also studied.

The bulk densities of the samples were measured by the Archimedes method. The phase purity of the sintered samples was examined by X-ray diffraction (XRD) techniques. The dielectric properties such as dielectric constant and unloaded quality factor were measured using an HP 8510 C Network Analyzer equipped with a sweep oscillator and test unit. The dielectric constant ($\varepsilon_r$) was obtained from the TE$_{011}$ resonant mode under end-shorted conditions and the quality factor ($Q_0$) by the cavity method. The temperature coefficient of resonant frequency ($\tau_f$) was measured by noting the temperature variation of TE$_{011}$ resonance mode in the temperature range 25-70°C.

The system Ca$_5$A$_2$TiO$_{12}$ (A=Nb, Ta) belongs to the complex perovskite family and can be conveniently written as Ca(Ca$_{114}$A$_{2/4}$Ti$_{1/4}$)O$_3$ with 1:2:1 ordering. Figure 1 shows the XRD patterns of Ca$_5$Nb$_2$TiO$_{12}$ and Ca$_5$Ta$_2$TiO$_{12}$ powdered ceramics. The XRD patterns are similar for both materials with a slight shift in the peak positions. Both these materials have orthorhombic symmetry.

The lattice parameters for Ca$_5$Nb$_2$TiO$_{12}$ are $a = 5.5104$ Å, $b = 7.9079$ Å and $c = 5.6880$ Å with a theoretical density of 4.19 g/cm$^3$. However, for Ca$_5$Ta$_2$TiO$_{12}$ they are $a = 5.5022$ Å, $b = 7.8931$ Å and $c = 5.6685$ Å with a theoretical density of 5.41 g/cm$^3$. The synthesising conditions such as calcination temperature, sintering temperature and their durations were optimized for both materials to obtain the best dielectric properties. The best density and dielectric properties of Ca$_5$Nb$_2$TiO$_{12}$ ceramics are obtained at a calcination temperature of 1350°C/4h and sintering temperature of 1550°C/4h. In the case of Ca$_5$Ta$_2$TiO$_{12}$ ceramics the optimum calcination temperature is the same as that of the niobates but the sintering temperature is 1625°C/4h (see Figs. 2 to 4).

The density and dielectric properties decrease above and below the optimum calcination temperature. Incomplete reactions and intermediate phases may be the reason for poor dielectric properties and density below the optimum calcination temperature. At temperatures well above the optimum calcination temperature grain growth will occur even during calcination, which is detrimental to the density and dielectric properties.

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**Fig. 1.** XRD patterns of (a) Ca$_5$Nb$_2$TiO$_{12}$ and (b) Ca$_5$Ta$_2$TiO$_{12}$ ceramics.
Nomura et al.\textsuperscript{7} reported that small Mn\textsuperscript{4+} addition in some titanate based ceramics, such as Ba\textsubscript{2}Ti\textsubscript{9}O\textsubscript{20}, increased their density and improved the dielectric properties. This is due to the fact that Mn will act as an oxidizing agent in the sintering process and will enhance the value of $Q_a$. Hence, different mole% (0.2 to 5 mole%) of MnO\textsubscript{2} were added to Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} and Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12}. Although the density increased slightly by about 1%, the dielectric properties were found to be adversely affected.

In titanium based ceramics titanium is in Ti\textsuperscript{4+} oxidation state. It has been reported that prolonged heating at a temperature slightly less than the sintering temperature will cause the reduction of Ti\textsuperscript{4+} to Ti\textsuperscript{3+} which may improve the density and dielectric properties. Hence, we have annealed Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} samples at a temperature of 1350°C, followed by annealing at 1150°C for 15 h each. Similarly, Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} was annealed at 1450°C and 1250°C for 15 h each. This resulted in the decrease of density, dielectric constant and $Q_a$ while $\tau_f$ increased slightly.

Figure 2: Variation of density of Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} and Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} ceramics with calcination temperature.

Figure 3: Variation of dielectric properties of Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} as a function of sintering temperature.

Figure 4: Variation of dielectric properties of Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} as a function of sintering temperature.

Table I. Density and dielectric properties of Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} and Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} under optimum synthesising conditions, after annealing and doping of MnO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bulk density (g/cm\textsuperscript{3})</th>
<th>Dielectric constant $\varepsilon_r$</th>
<th>$Q_a \times f$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12}</td>
<td>4.048</td>
<td>48</td>
<td>26600</td>
<td>+40</td>
</tr>
<tr>
<td>Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12}</td>
<td>4.087</td>
<td>48</td>
<td>24390</td>
<td>+42</td>
</tr>
<tr>
<td>Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12}</td>
<td>4.033</td>
<td>47</td>
<td>23200</td>
<td>+44</td>
</tr>
<tr>
<td>Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12}</td>
<td>5.258</td>
<td>38</td>
<td>33100</td>
<td>+10</td>
</tr>
<tr>
<td>Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12}</td>
<td>5.267</td>
<td>38</td>
<td>28800</td>
<td>+12</td>
</tr>
<tr>
<td>Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12}</td>
<td>5.258</td>
<td>38</td>
<td>30430</td>
<td>+12</td>
</tr>
</tbody>
</table>

a) Pure  
b) 1 mole% MnO\textsubscript{2}  
c) Annealed

In conclusion, Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} and Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} ceramics were prepared as single-phase materials by a conventional solid-state ceramic process. Microwave dielectric properties of Ca\textsubscript{5}A\textsubscript{2}TiO\textsubscript{12} (A=Nb, Ta) have been reported for the first time. Ca\textsubscript{5}Nb\textsubscript{2}TiO\textsubscript{12} has $\varepsilon_r = 48$, $Q_a \times f > 25000$ GHz and $\tau_f = +40$ ppm/°C. Ca\textsubscript{5}Ta\textsubscript{2}TiO\textsubscript{12} has $\varepsilon_r = 38$, $Q_a \times f > 30000$ GHz and $\tau_f = +10$ ppm/°C. Annealing at lower temperatures and the addition of dopants such as Mn have no significant effect on the microwave dielectric properties. The properties of these materials indicate that they can be used for dielectric resonator applications in microwave communication systems and as substrates in microelectronic technology.

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