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Short Note

Synthesis, Characterization and Properties of $Ca_5A_2TiO_{12}$ (A=Nb, Ta) Ceramic Dielectric Materials for Applications in Microwave Telecommunication Systems

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Microwave ceramic dielectric materials $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ have been prepared by a conventional solid-state ceramic process. The structure was studied by X-ray diffraction and the dielectric properties were characterized at microwave frequencies. The ceramics posses a relatively high dielectric constant, very low dielectric loss ($Q_u \times f > 30000$ GHz) and small temperature variation of resonant frequency. These materials are potential candidates for dielectric resonator applications in microwave integrated circuits. [DOI: 10.1143/JJAP.41.3834]

KEYWORDS: dielectric materials, dielectric resonators, microwave ceramics, complex perovskites, microwave resonators

Revolutionary progress in the field of microwave communication has lead to the invention of several dielectric resonator (DR) materials[1)] which are indispensable components in almost all modern telecommunication systems. High dielectric constant materials are very important in microelectronic technologies such as dynamic random access memory (DRAM)[2)] devices, substrates for microwave integrated circuits (MIC) and as gate dielectrics. Recently, Cava *et al.*[3)] reported the low-frequency (1 MHz) dielectric properties of the system $Ca_5A_2TiO_{12}$ (A=Nb, Ta). In the present paper, we report the microwave dielectric properties of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ 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 $Ca_5A_2TiO_{12}$ (A=Nb, Ta) were prepared by a conventional solid-state ceramic process. Stoichiometric amounts of high-purity $CaCO_3$, TiO_2, Nb_2O_5/Ta_2O_5 were weighed and ball milled using zirconia balls in distilled water medium for 24 h. The mixture was dried and calcined at temperatures in the range 1200–1400°C for 4 h each. The calcined powders were again well ground 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, ground again 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 1 h to expel the binder. $Ca_5Nb_2TiO_{12}$ samples were sintered in the temperature range 1500–1600°C and $Ca_5Ta_2TiO_{12}$ 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 (ε_r) was obtained from the TE_{011} resonant mode under end-shorted conditions[4)] and the quality factor (Q_u) by the cavity method.[5)] The temperature coefficient of resonant frequency (τ_f) was measured by noting the temperature variation of $TE_{01\delta}$ resonance mode in the temperature range 25–70°C.

The system $Ca_5A_2TiO_{12}$ (A=Nb, Ta) belongs to the complex perovskite family and can be conveniently written as $Ca(Ca_{1/4}A_{2/4}Ti_{1/4})O_3$ with 1 : 2 : 1 ordering. Figure 1 shows the XRD patterns of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ powdered ceramics. The XRD patterns are similar for both materials with a slight shift in the peak positions. Both these materials have orthorhombic symmetry.[6)]

The lattice parameters for $Ca_5Nb_2TiO_{12}$ 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 $Ca_5Ta_2TiO_{12}$ 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 $Ca_5Nb_2TiO_{12}$ ceramics are obtained at a calcination temperature of 1350°C/4 h and sintering temperature of 1550°C/4 h. In the case of $Ca_5Ta_2TiO_{12}$ ceramics the optimum calcination temperature is the same as that of the niobates but the sintering temperature is 1625°C/4 h (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.

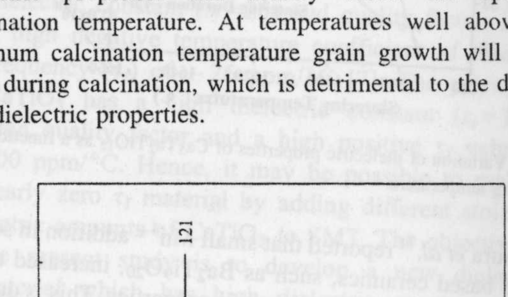

Fig. 1. XRD patterns of (a) $Ca_5Nb_2TiO_{12}$ and (b) $Ca_5Ta_2TiO_{12}$ ceramics.

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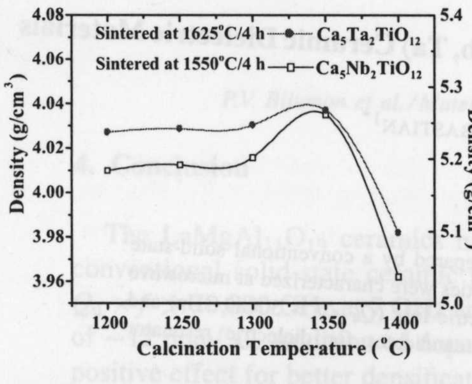

Fig. 2. Variation of density of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ ceramics with calcination temperature.

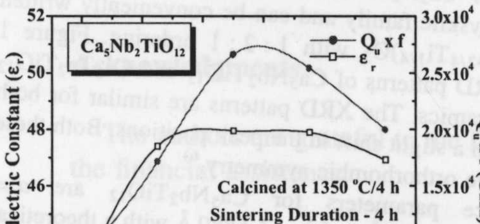

Fig. 3. Variation of dielectric properties of $Ca_5Nb_2TiO_{12}$ as a function of sintering temperature.

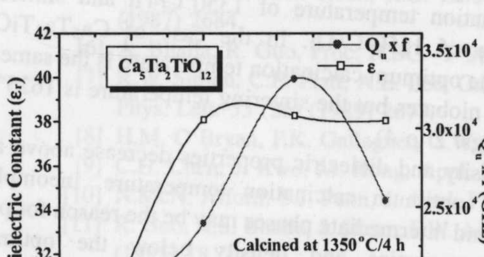

Fig. 4. Variation of dielectric properties of $Ca_5Ta_2TiO_{12}$ as a function of sintering temperature.

Nomura *et al.*[7] reported that small Mn^{4+} addition in some titanate based ceramics, such as $Ba_2Ti_9O_{20}$, 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_u. Hence, different mole% (0.2 to 5 mole%) of MnO_2 were added to $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$. 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^{4+} oxidation state. It has been reported that[7] prolonged heating at a temperature slightly less than the sintering temperature will cause the reduction of Ti^{4+} to Ti^{3+} which may improve the density and dielectric properties. Hence, we have annealed

Table I. Density and dielectric properties of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ under optimum synthesising conditions, after annealing and doping of MnO_2.

Material	Bulk density (g/cm^3)	Dielectric constant (ε_r)	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
$Ca_5Nb_2TiO_{12}$ a)	4.048	48	26600	+40
$Ca_5Nb_2TiO_{12}$ b)	4.087	48	24390	+42
$Ca_5Nb_2TiO_{12}$ c)	4.033	47	23200	+44
$Ca_5Ta_2TiO_{12}$ a)	5.258	38	33100	+10
$Ca_5Ta_2TiO_{12}$ b)	5.267	38	28800	+12
$Ca_5Ta_2TiO_{12}$ c)	5.258	38	30430	+12

a) Pure
b) 1 mole% MnO_2
c) Annealed

$Ca_5Nb_2TiO_{12}$ samples at a temperature of 1350°C, followed by annealing at 1150°C for 15 h each. Similarly, $Ca_5Ta_2TiO_{12}$ was annealed at 1450°C and 1250°C for 15 h each. This resulted in the decrease of density, dielectric constant and Q_u while τ_f increased slightly.

The sintered samples were kept in boiling water for 2 h. There was no change in density, dielectric properties or in the XRD pattern, indicating the excellent chemical and thermal stability of the material. Cava *et al.*[3] reported the dielectric constant of $Ca_5Nb_2TiO_{12}$ to be 35 and that of $Ca_5Ta_2TiO_{12}$ to be 23. The ceramic samples prepared by us have more than 96% of their theoretical density. The dielectric constant in the present work measured in the 4–6 GHz range is about 30% higher than that reported by Cava *et al.* at 1 MHz which may be due to the higher sintered density of our samples. Table I lists the density and microwave dielectric properties of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ resonators.

In conclusion, $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ ceramics were prepared as single-phase materials by a conventional solid-state ceramic process. Microwave dielectric properties of $Ca_5A_2TiO_{12}$ (A=Nb, Ta) have been reported for the first time. $Ca_5Nb_2TiO_{12}$ has $\varepsilon_r = 48$, $Q_u \times f > 25000$ GHz and $\tau_f = +40$ ppm/°C. $Ca_5Ta_2TiO_{12}$ has $\varepsilon_r = 38$, $Q_u \times f > 30000$ 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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