

Microwave dielectric properties of temperature stable $\text{Ca}_5\text{A}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($A = \text{Nb, Ta}$) ceramics

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Abstract $\text{Ca}_5\text{A}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($A = \text{Nb, Ta}$) ceramics have been prepared as single-phase materials by conventional solid-state ceramic route. Their structure and microstructure were studied by X-ray diffraction and scanning electron microscopic methods and dielectric properties were characterised in the 4–6 GHz microwave frequency range. We observed an increase in cell volume and theoretical density with compositional variations. In $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics the dielectric constant varied from 48 to 22 and quality factor from 26000 to 16000 GHz whereas in $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ the variation in dielectric constant was from 38 to 17 and quality factor from 33000 to 18000 GHz with increase in x . In both the ceramic systems the temperature coefficient of resonant frequency shifted from positive to negative values with Hf^{4+} substitution for Ti^{4+} .

Keywords Dielectric resonators · Microwave ceramics · Complex perovskites · Solid solution · Powder diffraction · Dielectric properties

1. Introduction

The growth of telecommunication industry over the past decade has resulted in an increasing demand for the miniatur-

ization of wireless and microwave devices. Being an integral part of most of the microwave devices as filters, oscillators and antennas, dielectric resonators (DRs) [1] play a vital role in the miniaturization of practical circuits [2–4] because of their high dielectric constant (ϵ_r) compared with air filled metallic cavities. Moreover DRs with high unloaded quality factor (Q_u) and low temperature coefficient of resonant frequency (τ_f) are essential for efficiency, selectivity and stability of the microwave circuits. Several DR materials [5] have been reported by various research groups. But owing to the difficulty in controlling the dielectric properties at microwave frequencies intense work is going on in search of new materials and tailoring [6–9] the properties of existing ones with improved properties.

Low loss $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ ceramics [10] have recently attracted much attention because of their interesting dielectric properties. The materials belong to a special category of complex perovskite with the mixing of three cations in the B -site in the 1:2:1 ratio when represented in the usual perovskite form as $\text{Ca}(\text{Ca}_{1/4}\text{Nb}_{1/2}\text{Ti}_{1/4})\text{O}_3$ and $\text{Ca}(\text{Ca}_{1/4}\text{Ta}_{1/2}\text{Ti}_{1/4})\text{O}_3$. Extensive researches were carried out [11, 12] to probe into the complexity of structure, microstructure and cation ordering in these ceramics. The Nb and Ta-based materials have the same crystal structure and are orthorhombic with $Pnma$ space group. Recently Bijumon et al. [13, 14] reported the microwave dielectric properties of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ ceramics. $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ has $\epsilon_r = 48$, $Q_u \times f > 26000$ (at 4 GHz) and $\tau_f = +40$ ppm/°C, whereas $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ has $\epsilon_r = 38$, $Q_u \times f > 33000$ (at 4.5 GHz) and $\tau_f = +10$ ppm/°C when sintered at 1550°C/4 h and 1625°C/4 h respectively. Investigations were also made to tailor the microwave dielectric properties of these ceramics by solid solution formations [15, 16] doping [17] and glass fluxing [18]. Both these materials have found applications in the fabrication of broadband antennas. $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$

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was found to be effective in making a 5 fold increase in the bandwidth of a DR loaded rectangular microstrip patch antenna [19] and the same material was used for the fabrication of wide band cylindrical [20] and rectangular [21] dielectric resonator antennas. $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ has been used to develop stacked monopole-dielectric resonator wideband antennas [22]. Though the materials have been proved good for practical purposes, the relatively high τ_f value precludes their immediate use in microwave devices. Hence the main objective of the present investigation was to improve the τ_f of $\text{Ca}_5\text{A}_2\text{TiO}_{12}$ ($A = \text{Nb}, \text{Ta}$) ceramics by suitable substitutions. In the present paper we report the microwave dielectric properties of $\text{Ca}_5\text{A}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($A = \text{Nb}, \text{Ta}$) solid solution phases.

2. Experimental details

$\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics were synthesized using the conventional solid-state reaction method. The starting materials were high purity (>99.9%) CaCO_3 , TiO_2 , HfO_2 (Aldrich Chemicals, Milwaukee WI, USA), and $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ (Nuclear Fuel Complex, Hyderabad, India). Stoichiometric amounts of initial raw materials were mixed by ball milling for 24 h with yttria stabilized ZrO_2 balls in distilled water, and then dried and calcined at $1350^\circ\text{C}/4$ h. The calcined powders were well ground in an agate mortar with pestle and mixed with 4 wt% poly vinyl alcohol (PVA) as binder and dried again. It was well ground to form fine powder and shaped into cylindrical compacts of about 14 mm diameter and 7 mm height under a pressure of about 100 MPa. Each composition was sintered at their optimum temperatures (See Table 1). Compositions with

$x = 0.8$ and 1 were difficult to sinter even at 1700°C and hence were sintered with the addition of 2 wt % B_2O_3 .

The bulk densities of well-polished samples were measured by Archimedes method. X-Ray diffraction patterns were recorded from powders obtained by crushing the sintered specimens ($\text{CuK}\alpha$ radiation, Philips X-Ray Diffractometer, Netherlands). The polished surfaces of the ceramics were investigated by scanning electron microscopy (SEM, Model S-2400, Hitachi, Japan) after thermal etching. The unloaded quality factor was measured by resonance method using a metallic cavity [23] interfaced with a reflection/transmission network analyser (Model 8753 ET, Agilent Technologies Inc. Palo Alto, CA). The measurements were made in the transmission mode using the $TE_{01\delta}$ resonant mode. The ϵ_r was calculated using TE_{011} resonant mode of the sample by keeping it under end-shortened condition using two finely polished gold coated copper plates as proposed by Hakki and Coleman [24] and later modified by Courtney [25]. The τ_f was measured by noting the temperature variation of TE_{011} resonance mode in the temperature range $25\text{--}70^\circ\text{C}$.

3. Results and discussion

3.1. Phase analysis

Figures 1 and 2 show the X-Ray diffraction patterns of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ for $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 respectively. The XRD patterns of both the systems are similar and differ only in a slight shift in the position of diffraction peaks. A perovskite single phase with the same structure as that of the parent materials were obtained for compositions up to $x = 0.6$. However,

Table 1 Sintering temperature, unit cell parameters, density and tolerance factor of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics

Material	x	Sintering Temperature ($^\circ\text{C}/4$ h)	Lattice parameters (Standard Deviation SD = 0.002 Å)			Cell Volume (Å^3)	X-Ray Density (g/cm^3)	% Density	Tolerance Factor (t)
			a (Å)	b (Å)	c (Å)				
$\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$	0.0	1550	5.510	7.908	5.688	247.84	4.19	96.9	0.919
	0.2	1580	5.531	7.930	5.674	248.87	4.35	96.2	0.917
	0.4	1625	5.547	7.955	5.656	249.59	4.51	96.0	0.914
	0.6	1680	5.559	7.969	5.661	250.78	4.64	95.4	0.912
	0.8	1650 [#]	5.565	7.977	5.669	251.66	4.82	94.2	0.910
	1.0	1675 [#]	5.574	7.986	5.671	252.44	4.97	93.4	0.908
$\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$	0.0	1625	5.502	7.893	5.668	246.15	5.41	97.2	0.919
	0.2	1650	5.521	7.909	5.671	247.63	5.55	96.8	0.917
	0.4	1680	5.534	7.917	5.679	248.81	5.70	96.2	0.914
	0.6	1650 [#]	5.550	7.926	5.675	249.64	5.86	95.1	0.912
	0.8	1675 [#]	5.563	7.941	5.667	250.34	6.01	94.0	0.910
	1.0	1675 [#]	5.571	7.952	5.675	251.41	6.16	92.6	0.908

[#]Sintered with 2 wt % B_2O_3

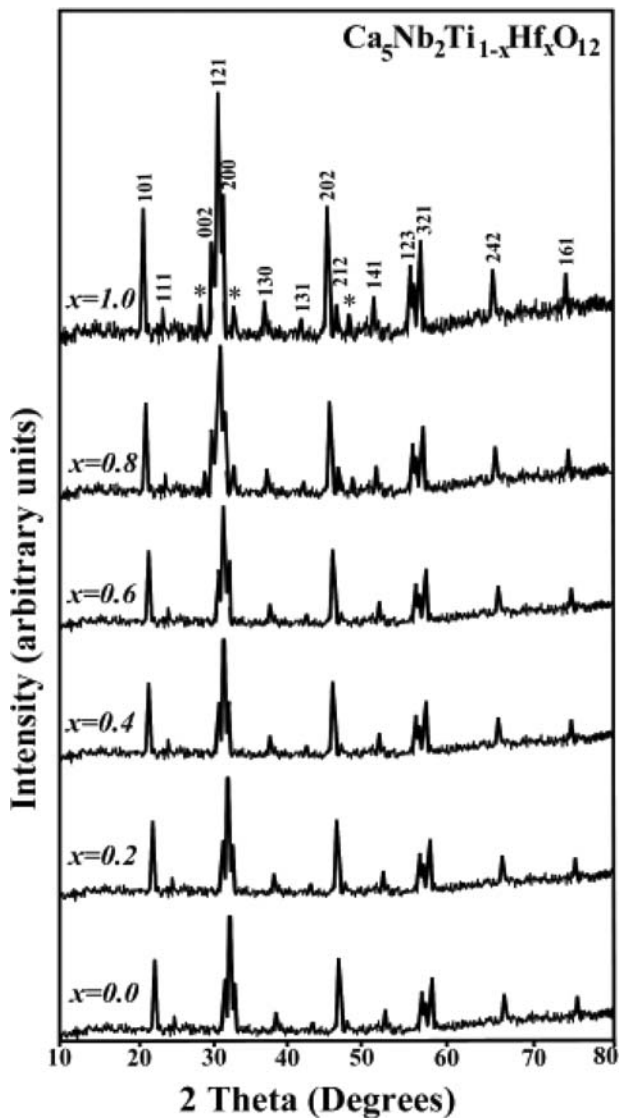


Fig. 1 X-Ray diffraction pattern of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics (*→ additional phases)

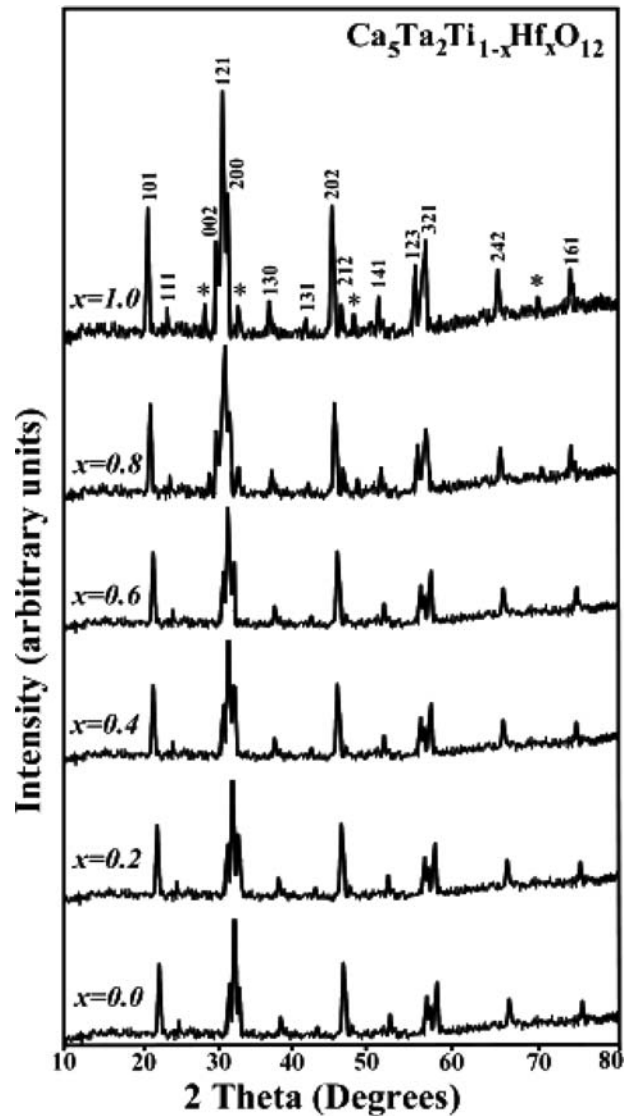


Fig. 2 X-Ray diffraction pattern of $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics (*→ additional phases)

compositions with $x = 0.8$ and 1.0 show few additional peaks of $\text{Ca}_2\text{B}_2\text{O}_5$ (ICDD File No. 22 – 139), which was formed when 2 wt % B_2O_3 was added as sintering aid. The diffraction peaks in Figs. 1 and 2 were indexed based on orthorhombic $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ phases respectively. A slight shift in the position of maximum intensity peaks [(121), (101) & (202)] towards the lower angle side was observed which was later confirmed by an increase in lattice parameters and associated increase in cell volume. This is due to the partial substitution of Hf ions for Ti in the perovskite B-site. The sintering temperatures, lattice parameters, cell volume, density and tolerance factors of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics are given in Table 1. As x increased from 0 to 1, the sintering temperature increased from 1550 to 1680°C/4 h. In both ceramic systems the sinterabil-

ity was very poor for compositions with $x = 0.8$ and 1.0 and hence were sintered with low melting B_2O_3 glass additives. It is known that effective low temperature sintering can be achieved by fluxing a ceramic material with a suitable glass in a suitable concentration [26]. Hence, dense ceramics at low sintering temperatures were expected with the addition of glass additives. However, it is observed that (See Table 1) the percentage density of B_2O_3 added compositions are less than that of compositions sintered without glass additives ($x = 0$ to 0.6). Though efforts were made to increase the densification by increasing the sintering temperatures, the ceramics could attain only 93 to 94 percentage of their theoretical density. As is evident from the XRD, B_2O_3 forms $\text{Ca}_2\text{B}_2\text{O}_5$ secondary phase with the matrix material and which in turn decreases the experimental density of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics (for $x = 0.8$ to 1). This is

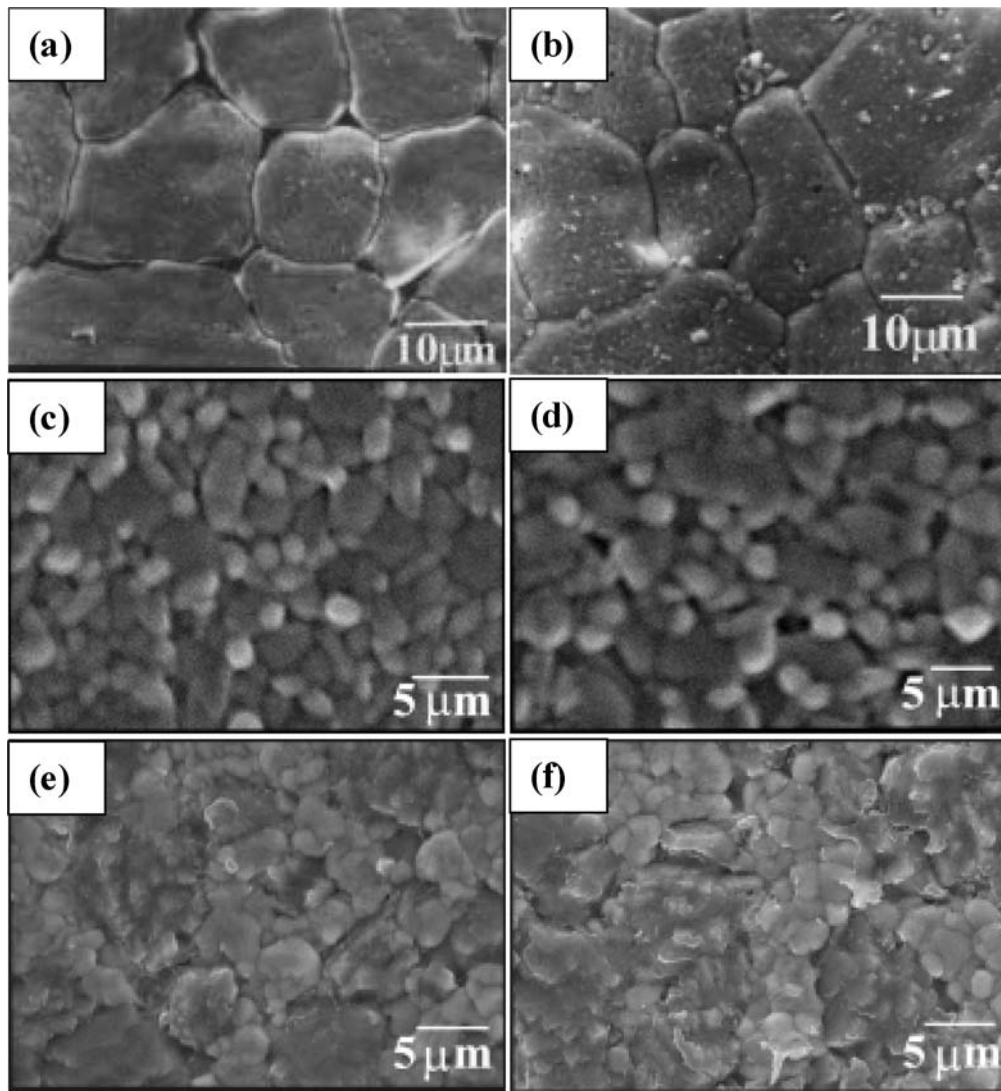


Fig. 3 SEM photographs of (a) $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ (b) $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ (c) $\text{Ca}_5\text{Nb}_2\text{Ti}_{0.4}\text{Hf}_{0.6}\text{O}_{12}$ (d) $\text{Ca}_5\text{Ta}_2\text{Ti}_{0.6}\text{Hf}_{0.4}\text{O}_{12}$ (e) $\text{Ca}_5\text{Nb}_2\text{HfO}_{12}$ and (f) $\text{Ca}_5\text{Ta}_2\text{HfO}_{12}$ ceramics

due to the lower density of $\text{Ca}_2\text{B}_2\text{O}_5$ (2.83 g/cm^3) [ICDD File No. 22–139] compared with that of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ [See Table 1] ceramics. The variation of unit cell parameters are listed in Table 1, which shows a linear increase with HfO_2 content. It can be attributed to the substitution of Hf^{4+} with higher ionic radius (0.71 \AA) [27] than Ti^{4+} (0.605 \AA) in the B-site of complex perovskite materials. Even with increased cell volume, the X-Ray density showed an increase with x and is due to the increased mass of Hf^{4+} ions compared with Ti^{4+} . But it should be noted that the percentage density decreased with increase in x and can be attributed to the poor sinterability of HfO_2 compared with that of TiO_2 . The tolerance factors (t) [28] of $\text{Ca}_5\text{A}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($A = \text{Nb, Ta}$) ceramics were calculated for $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 and is given in Table 1. A gradual decrease in t with increasing x can be seen and is due to the

increased average B-site ionic radius due to the substitution of bigger Hf^{4+} in place of Ti^{4+} ions.

3.2. Microstructural analysis

The surface morphology of few typical $\text{Ca}_5\text{A}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($A = \text{Nb, Ta}$) ceramics are depicted in Fig. 3. The SEM pictures of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ ceramics illustrated in Fig. 3(a) and 3(b) respectively show well-packed grains with an average size of $10 \mu\text{m}$. Fig. 3(c) and 3(d) are the SEM photographs for $\text{Ca}_5\text{Nb}_2\text{Ti}_{0.4}\text{Hf}_{0.6}\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{0.6}\text{Hf}_{0.4}\text{O}_{12}$ ceramics, where the dielectrics appeared as temperature stable. The specimens have a homogeneous microstructure and the average grain size is about $3 \mu\text{m}$ for both the ceramics. It should be noted that the grains are not well packed and leaves porosity confirming the decreased

percentage density with increase in x . It is noteworthy that the grain shape is uniform and is similar to that of the parent material, which shows that the ceramics form solid solution in the $\text{Ca}_5\text{A}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ composition. Fig. 3(e) and 3(f) exhibit SEM images recorded from the thermally etched surfaces of $\text{Ca}_5\text{Nb}_2\text{HfO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{HfO}_{12}$ ceramics respectively. A large amount of liquid phase can be seen coated over the grains. The B_2O_3 – based glassy material coated the grains of the matrix and reacted with the host materials to form a glass based low melting phase. The presence of $\text{Ca}_2\text{B}_2\text{O}_5$ secondary phase and the poor sinterability of the ceramics for $x = 1$ resulted in a lower percentage density of about 93% of its theoretical value. A similar microstructure was observed for $\text{Ca}_5\text{Nb}_2\text{Ti}_{0.2}\text{Hf}_{0.8}\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{0.2}\text{Hf}_{0.8}\text{O}_{12}$ ceramics (for $x = 0.8$), which too was fluxed with glass to enhance sinterability.

3.3. Microwave dielectric properties

Variation of quality factor, dielectric constant and temperature coefficient of resonant frequency with x in $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics are shown in Figs. 4 and 5 respectively. In $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$, the $Q_u \times f$ decreased from 26000 to 16000 GHz and in the tantalum analogue the variation was from 33000 to 18000 GHz. In general, dielectric loss mechanisms can be divided into (i) intrinsic loss by anharmonic interaction with the microwave field and (ii) extrinsic loss by porosity and presence of secondary phases. In the present case, the substitution of Hf^{4+} ions for Ti^{4+} has decreased the percentage density of the ceramics and hence contributed towards the extrinsic loss with a resultant decrease in quality factor with increased x .

The ϵ_r of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ decreased from 48 to 22 and that of $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics decreased from 38 to 17. In both cases the porosity corrected ϵ_r was calculated [29] using the equation

$$\epsilon' = \epsilon_m \left[1 - \frac{3P(\epsilon_m - 1)}{2\epsilon_m + 1} \right]$$

where ϵ' is the experimental dielectric constant of the composite sample which contains a porosity P and ϵ_m is the porosity corrected dielectric constant of the material. In $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($0 \leq x \leq 1$) ceramics, the porosity corrected ϵ_r decreased from 51 to 29 and in $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($0 \leq x \leq 1$) ceramics the variation was from 40 to 22. Dielectric constant significantly depends on the percentage densification and ionic polarization [30] at microwave frequencies [31]. ϵ_r being directly related to ionic polarisability, an increase was expected with Hf^{4+} content since its polarisability is higher than that of Ti^{4+} . However, it is surprising that the porosity corrected ϵ_r also decreased by the substitution of Hf.

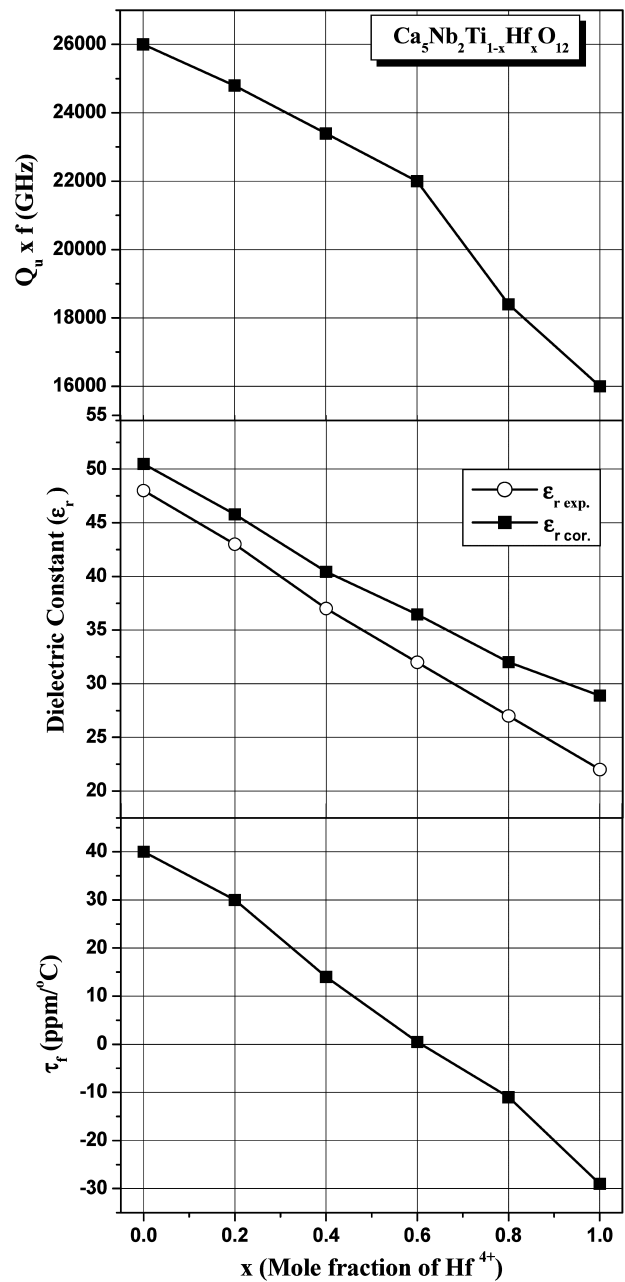


Fig. 4 Microwave dielectric properties of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics

Cationic substitutions have been employed [9, 15] as a major tool to tune the temperature coefficient of resonant frequency of microwave ceramics. In both the $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ systems, τ_f decreased with increase in x . In $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics τ_f decreased from +40 to -30 ppm/°C as x varied from 0 to 1. The τ_f becomes zero at $x = 0.6$. In $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics, the τ_f decreased from +10 to -32 ppm/°C with the zero τ_f at $x = 0.4$. The nearly linear variation of dielectric properties with $x = 0$ to 1 indicate that the addition of B_2O_3 for $x = 0.8$ and 1 do not considerably affect the properties.

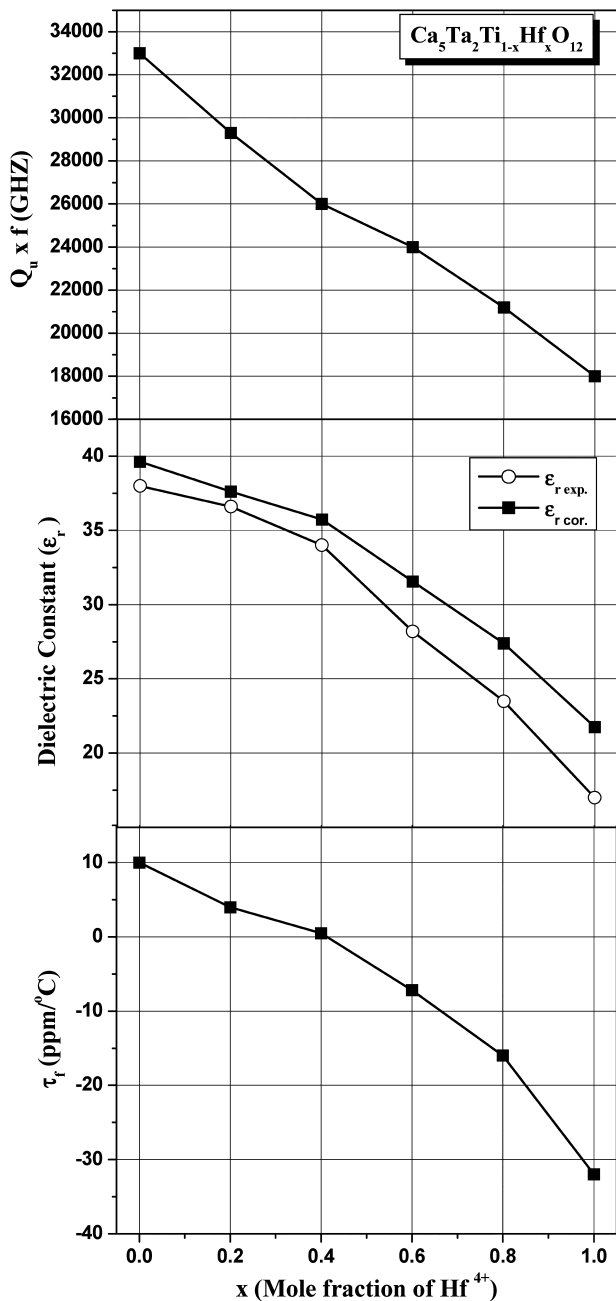


Fig. 5 Microwave dielectric properties of $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ceramics

4. Conclusions

The microwave dielectric properties of $\text{Ca}_5\text{Nb}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{Ti}_{1-x}\text{Hf}_x\text{O}_{12}$ ($0 \leq x \leq 1$) complex perovskites have been investigated. Single-phase ceramics with orthorhombic symmetry have been obtained for $x = 0.0$ to 0.6 . However $\text{Ca}_2\text{B}_2\text{O}_5$ secondary phase appeared for compositions $x = 0.8$ – 1.0 for which B_2O_3 was added as a sintering aid. A gradual decrease of quality factor and dielectric con-

stant was observed with increase in concentration of Hf^{4+} ions, whereas the temperature coefficient of resonant frequency was shifted from positive to negative values. The $\text{Ca}_5\text{Nb}_2\text{Ti}_{0.4}\text{Hf}_{0.6}\text{O}_{12}$ has $\epsilon_r = 32$, $Q_u x f = 22000$ (at 4.46 GHz) and $\tau_f = \pm 0.5$ ppm/°C and $\text{Ca}_5\text{Ta}_2\text{Ti}_{0.6}\text{Hf}_{0.4}\text{O}_{12}$ has $\epsilon_r = 34$, $Q_u x f = 26000$ (at 4.35 GHz) and $\tau_f = \pm 0.5$ ppm/°C. These temperature stable ceramics may be useful for dielectric resonator applications in the S and C band of microwave telecommunication devices.

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