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Tailoring the microwave dielectric properties of $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ ceramics

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Abstract

Microwave dielectric ceramics based on $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ have been prepared by conventional solid state method. The $GdTiTaO_6$ and $SmTiTaO_6$ have aeschenite structure with positive τ_f and $GdTiNbO_6$ and $YTiTaO_6$ have euxenite structure with negative τ_f. The τ_f of the ceramics has been tuned by preparing solid solution phases between the aeschynites and euxenites for a possible zero τ_f material. It is observed that $GdTiNb_{1-x}Ta_xO_6$ undergoes a phase transition from aeschynite to euxenite when $x = 0.75$ and in $Sm_{1-x}Y_xTiTaO_6$ for $x = 0.73$. The microwave dielectric properties change abruptly near the transition region. The τ_f value approaches zero near the phase transition region while the samples have poor sinterability and poor quality factor. The unloaded quality factor, dielectric constant and the sign of τ_f of the solid solution phases are found to depend on the average ionic radius of the rare earth ion in $RE_{1-x}RE'_xTiTaO_6$. The boundary of the euxenite-aeschynite phase transition occurs at an average (RE) ionic radius of 0.915 Å in $Sm_{1-x}Y_xTiTaO_6$ solid solution phases.

Keywords: Dielectric properties; Dielectric resonator; Microwave ceramics; Phase transition; Structure–property relation

1. Introduction

The development of microwave dielectric resonators for communication systems such as cellular telephones and global positioning systems has been rapidly growing in the past decade. The advantage of using dielectric resonators is that it enhances size reduction and cost effectiveness of the microwave components used in filters and oscillators. The general requirements for a dielectric resonator are high dielectric constant ε_r (20–100), high unloaded quality factor Q_u (>2000) and low temperature coefficient of resonant frequency τ_f (<5ppm/°C). These three key parameters respectively correspond to the size reduction, frequency selectivity and temperature stability of the system.[1] To satisfy the demands of microwave circuit designs, each dielectric property requires precise control. Many materials prepared over the years[2–8] have high dielectric constant and quality factor, but the optimal controlling of the temperature coefficient of resonant frequency stands out as one of the most difficult challenge to a material scientist.

The orthorhombic ternary oxides of the type $RE(AB)O_6$ [$A = $Ti, Hf; $B = $Ta, Nb] has been studied by several investigators[9–16] who were in search of stable high melting materials with low thermal expansivity. Later on Qi et al.[17–20] found out that these dielectric ceramics can be used as ideal gain media for miniature solid state lasers because of their exciting optical properties. Until recently, the versatility of the niobate compounds of rare earth elements with titanium based on $RETiNbO_6$ was not properly explored when Sebastian et al.[21] reported that these materials are ideal for dielectric resonator applications. The $RETiNbO_6$ compounds with atomic number of the rare earth ion in the range 57 to 63 in the periodic table were reported [32–34] to crystallize in orthorhombic structure with space group Pnma, $Z = 4$ and are isostructural with minerals of the aeschynite-priorite group. The aeschynites are reported[22] to have high dielectric constant and positive τ_f. The compounds with RE atomic number 64–71 showed an additional high temperature form isostructural with euxenite[17] polycrase minerals having space group Pbcn. They have comparatively lower dielectric constant and negative τ_f.[16,21] Very recently, a

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comprehensive investigation on a new group of dielectric resonators based on $RETiTaO_6$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In) has been made by Surendran et al.[22] who reported that these ceramics were superior to their niobium counterparts because of their relatively higher unloaded quality factor in the C (4–6 GHz) microwave frequency band. The $RETiTaO_6$ ceramics with RE ions with atomic number between 58 and 66 exhibit an aeschynite orthorhombic Pnma $\left(D_{2h}^{16}\right)$ structure, with four molecules per unit cell which showed high dielectric constant and positive τ_f. The compounds with Y and RE atomic number higher than 67, exhibit an euxenite orthorhombic Pbcn $\left(D_{2h}^{14}\right)$ structure and these materials showed low dielectric constant and negative τ_f .[14,16,22] A solid solution between aeschynites and euxenites by partially replacing one rare earth with another can tailor the τ_f to a minimum, which had been achieved successfully in $RETiNbO_6$ ceramics .[23,24] But a solid solution between $RETiTaO_6$ (aeschynite) and $RE'TiTaO_6$ (euxenite) and also between $RETiTaO_6$ (aeschynite) and $RETiNbO_6$ (euxenite) has not been attempted before. In this paper, we report the preparation, characterization and microwave dielectric properties of $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ [$x = 0.0$–1.0] ceramics. The range of solid solution formation and the effect of morphotropic phase transition from aeschynite to euxenite on the density and microwave dielectric properties of the solid solution phases were discussed.

2. Experimental

The $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ ceramics were prepared by the conventional solid-state ceramic route. The oxides of rare earths, titanium and niobium/tantalum were weighed in appropriate molar ratio and ball milled in a polyethylene bottle with zirconia balls using distilled water as the mixing medium. The slurry was dried at 100 °C in a hot air oven and was calcined in platinum crucibles at 1250 °C for 8 h in air with intermediate grinding. The calcined powder was ground in an agate mortar for several hours and then 3 wt.% of poly vinyl alcohol (PVA) was added as binder. The slurry was mixed well, dried and once again ground for 1 h before being formed into cylindrical compacts of about 14 mm diameter and 6–8 mm thickness in tungsten carbide (WC) die under a pressure of about 200 MPa to maintain an aspect ratio of two. A 4 wt.% solution of stearic acid in propan 2-ol was used as a lubricant. These compacts were fired at a rate of 5 °C/min up to 500 °C and soaked at 500 °C for 1 h to expel the binder. The pellets were sintered for 4 h in air on platinum plates at a heating rate of 10 °C/min. The sintering temperature for $GdTiNb_{1-x}Ta_xO_6$ was in the range 1520–1540 °C and that of $Sm_{1-x}Y_xTiTaO_6$ was 1550–1625 °C. After sintering, the samples were allowed to cool down to room temperature at a rate of 5 °C/min. The well-polished ceramic pellets with aspect ratio (D/L) of about two were used for microwave measurements. The bulk densities of the sintered samples were measured using Archimedes' method. The phase distribution of the powdered samples were analyzed by an X-ray diffractometer (Rigaku-Dmax 1C, Japan) using CuK_α radiation. The polished thin pellets were electroded by coating silver paste on both sides in the form of ceramic capacitors and were used for dielectric measurements at low frequencies (50 Hz–13 MHz) using an impedance analyzer (HP 4102 A-LF).

The dielectric properties such as dielectric constant ε_r and quality factor Q_u of the dielectric material were measured in the microwave frequency range using a vector network analyzer HP 8510 C, an HP 8514 test unit and an HP 8341 B sweep oscillator. The dielectric constant ε_r was measured by the post resonator method of Hakki and Coleman[25] using $TE_{01\delta}$ mode of resonance coupled through E-field probes as described by Courtney.[26] The unloaded quality factor Q_u of resonance was determined using a resonant cavity method proposed by Krupka et al. [27] The coefficient of thermal variation of resonant frequency τ_f was measured by noting the temperature variation of the resonant frequency of $TE_{01\delta}$ mode in the reflection configuration over a range of temperature 25–80 °C, keeping the dielectric in the end shorted position.

3. Results and discussion

The powder diffraction patterns recorded from $GdTiNb_{1-x}Ta_xO_6$ for $x = 0.0$, 0.6, 0.70. 0.72, 0.74, 0.76, 0.8 and 1.0 are given in Fig. 1. The $GdTiNbO_6$ crystallizes in orthorhombic euxenite structure having Pbcn $\left(D_{2h}^{14}\right)$ structure, with four formula units per unit cell.[16,21] The XRD pattern of $GdTiNbO_6$ is comparable with JCPDS file card number 27-1449 for $TbTiNbO_6$ and that of $GdTiTaO_6$ is comparable to JCPDS card number 28-1289 for $TbTiTaO_6$. It is evident from Fig. 1 that the XRD pattern of $GdTiNb_{1-x}Ta_xO_6$ ceramics is similar to that of euxenites for $x < 0.7$ and is similar to that of aeschynites for $x > 0.8$. The structural phase transition occurs between $x = 0.7$ and $x = 0.8$. In this range of x the $GdTiNb_{1-x}Ta_xO_6$ showed additional diffractions peaks, which could not be indexed using the powder diffraction patterns of the end members. The XRD pattern of $SmTiTaO_6$ is comparable to ICDD file number 28-1289 for $TbTiTaO_6$ with orthorhombic aeschynite structure and that of $YTiTaO_6$ is identical with ICDD file number 32-1452 with euxenite symmetry which is however different from the rest of the euxenite ceramics in $RETiTaO_6$. In $Sm_{1-x}Y_xTiTaO_6$ solid solution also the presence of multiphase is visible between

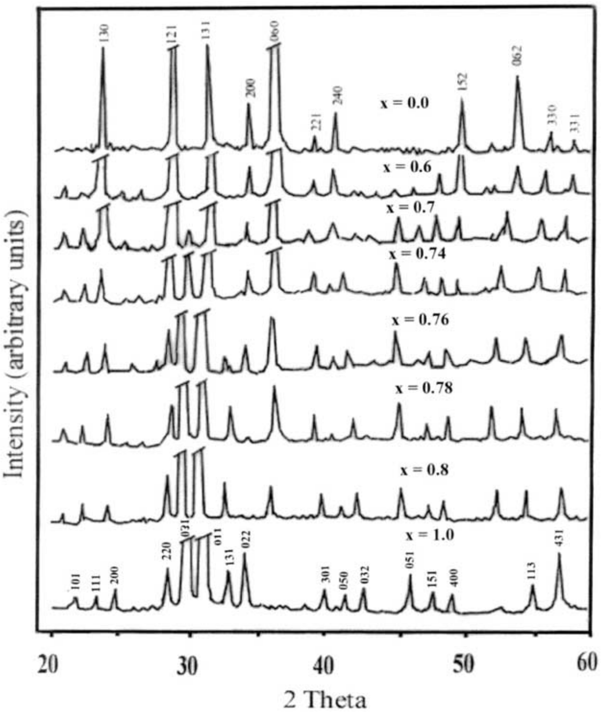

Fig. 1. Powder diffraction pattern of $GdTiNb_{1-x}Ta_xO_6$ for $x=0.0$, 0.7, 0.72, 0.74, 0.76, 0.78, 0.8 and 1.0.

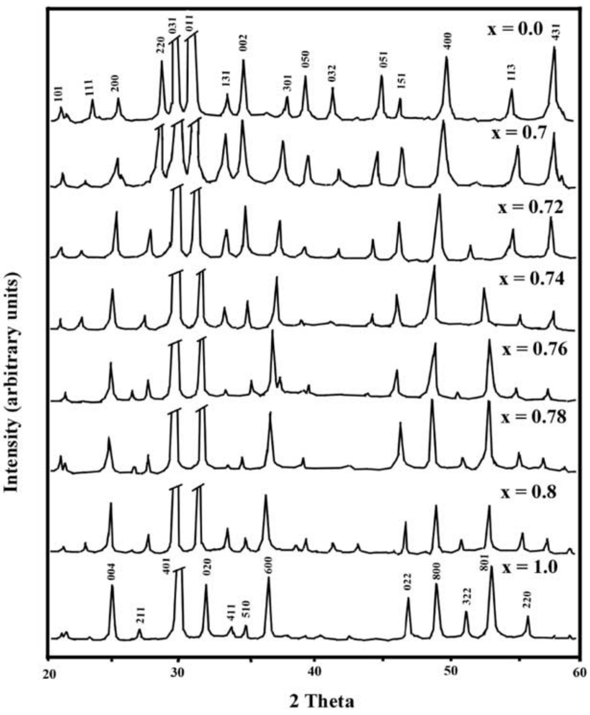

Fig. 2. Powder diffraction pattern of $Sm_{1-x}Y_xTiTaO_6$ for $x=0.0$, 0.7, 0.72, 0.74, 0.76, 0.78, 0.8 and 1.0.

$x=0.7$ and 0.8 (see Fig. 2). For $x<0.7$, the crystal structure is aeschynite and for $x>0.8$ euxenite structure prevails.

The variation of bulk density of $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ [$x=0.0$–1.0] as a function of x is given in Fig. 3. The theoretical density[21] of $GdTiNbO_6$ is 6.26 g/cm^3 while that of $GdTiTaO_6$ is 7.47 g/cm^3. Hence in the solid solution $GdTiNb_{1-x}Ta_xO_6$ the bulk density increase with x as tantalum replaces niobium ion except near the phase transition region ($x=0.75$) where they showed poor densification. Increasing the sintering temperature resulted in the melting of the samples. In aeschynites the rare earth ion lie in closely connected chains whereas in euxenite they lie on densely packed parallel planes.[17] Similar poor densification behaviour near the aeschynite to euxenite phase transition was observed[24] in [$RE_{1-x}RE'x$] $TiNbO_6$ [RE = Pr, Nd, Sm; RE′ = Gd, Dy, Y] ceramics. The theoretical density[22] of $SmTiTaO_6$ is 7.29 g/cm^3 while that of $YTiTaO_6$ is 6.38 g/cm^3. In $Sm_{1-x}Y_xTiTaO_6$ the density decreases with x because of the substitution of a lighter rare earth ion. In $Sm_{1-x}Y_xTiTaO_6$ solid solution the bulk density drops at about $x=0.73$ where the symmetry changes.

The dielectric constant of $GdTiNbO_6$ is 20 (at 6.27 GHz) while that of $GdTiTaO_6$ is 38 (at 5.21 GHz). The measured dielectric constants were corrected for porosity.[28] The variation of the dielectric constant of the solid solution phases with x is plotted in Fig. 4. The solid solution phases of $GdTiNb_{1-x}Ta_xO_6$ is expected to have dielectric constant values in between 20 and 38. With the substitution of Ta^{5+} at the Nb^{5+} the dielectric constant increases from 20 to 24. This is expected since the ionic polarisability of Nb^{5+} (=3.97) is less than that of Ta^{5+} ion (=4.73)[29] and the intrinsic dielectric constant of a material depends on the total ionic polarisability and unit cell volume of the constituent ions according to Claussius–Massotti equation.[30] Again for $x>0.8$ the dielectric constant increases from 37 to 38. The dielectric constant varies abruptly for values of x between 0.7 and 0.8. The volume of the unit cell calculated using the

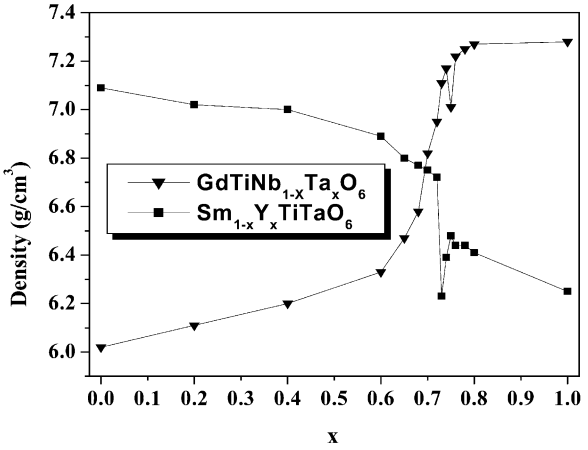

Fig. 3. Variation of bulk density of the solid solution phases with composition x.

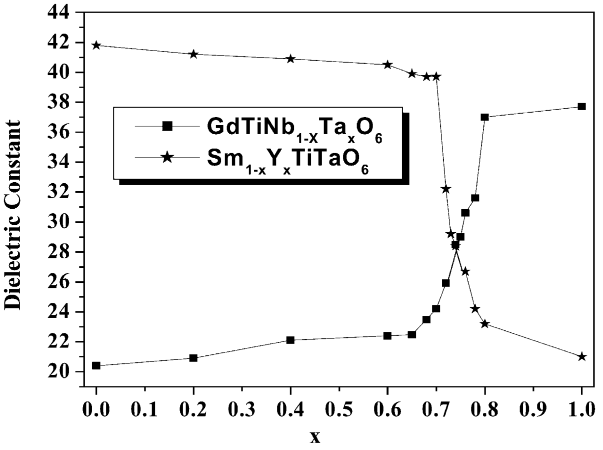

Fig. 4. Variation of dielectric constant of the solid solution phases with composition x.

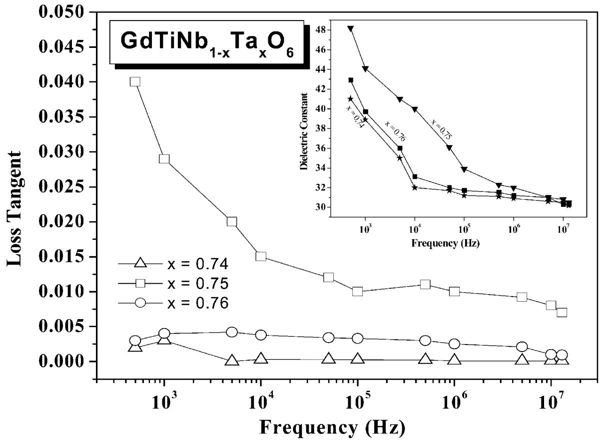

Fig. 6. Variation of the loss tangent and dielectric constant (inset) for $x=0.74$, 0.75 and 0.76 in $GdTiNb_{1-x}Ta_xO_6$ in the radio frequency range (10^2–1.3×10^7 Hz).

powder diffraction data recorded from $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ ceramics within the limits of experimental error is plotted against x in Fig. 5. The dielectric ceramic $GdTiNb_{0.25}Ta_{0.75}O_6$ could not be characterized by microwave method due to the very large dielectric loss factor (no resonance). Hence the solid solution compositions for $x=0.74$, 0.75 and 0.76 in $GdTiNb_{1-x}Ta_xO_6$ were characterized in the low frequency region (50 Hz–13 MHz) using an impedance analyzer. The dielectric constant of $GdTiNb_{0.25}Ta_{0.75}O_6$ ceramic was measured as 30.5 at 13 MHz (see Fig. 6). It is also evident that the dielectric loss factor for this ceramic is unusually high where the atoms are believed to be in a state of reorientation for a first order phase transformation from aeschynite to euxenite structure. The dielectric constant of $SmTiTaO_6$ is 42 (at 5.16 GHz) and that of $YTiTaO_6$ is 21 (at 6.23 GHz). The variation of dielectric of dielectric constant of $Sm_{1-x}Y_xTiTaO_6$ as a function of$x$is given in Fig. 4. The dielectric constant varies linearly up to $x=0.7$ and then again beyond $x=0.8$. The resonance vanishes for $x=0.73$ in $Sm_{1-x}Y_xTiTaO_6$ whose dielectric constant was measured as 29.9 at 13 MHz (see Fig. 7). The abnormal variation of the dielectric constant and dielectric loss factor for $x=0.75$ in $GdTiNb_{1-x}Ta_xO_6$ and $x=0.73$ in Sm_{1-x} Y_xTiTaO_6 with frequency is attributed to poor densification and the fact that the atoms are in a state of reorienation to form the new structure.

The variation of the temperature coefficient of resonant frequency τ_f with composition x is given in Fig. 8. In $GdTiNb_{1-x}Ta_xO_6$ the value of τ_f is -3 for $x=0.74$ and τ_f is $+2.6$ for $x=0.76$. A simple interpolation of the τ_f curve between $x=0.74$ and 0.76 showed that τ_f is near to zero for composition $x=0.75$. But it was not possible to measure it owing to the poor resonance in this region. Similarly in $Sm_{1-x}Y_xTiTaO_6$ ceramics it can be seen that τ_f is $+2.6$ for $x=0.72$ and -2 for $x=0.74$. The temperature coefficient approaches zero value for $x=0.73$. Thus it is expected that the resonant frequency is invariant with temperature for solid solution compo-

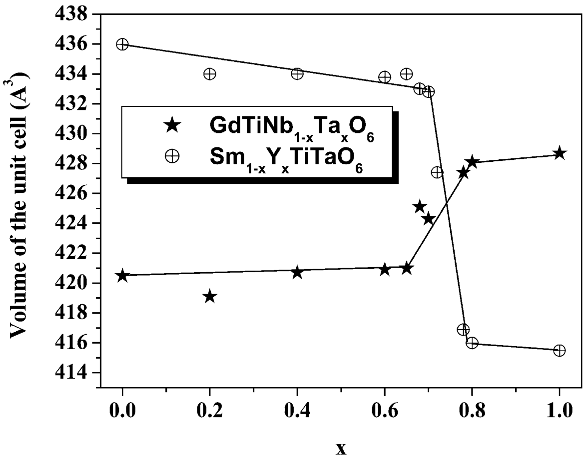

Fig. 5. Variation of unit cell volume of the solid solution phases in $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ [$x=0.0-1.0$] ceramics.

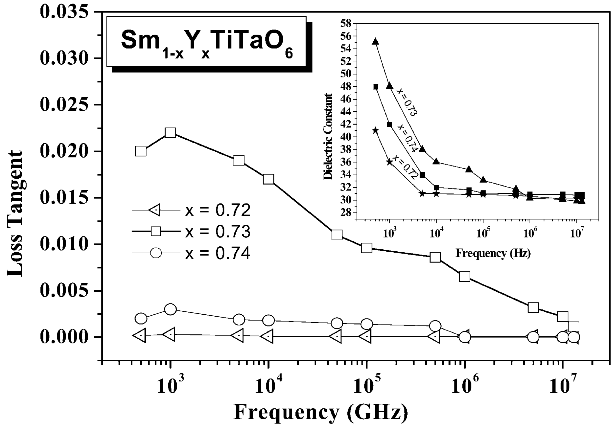

Fig. 7. Variation of the loss tangent and dielectric constant (inset) for $x=0.72$, 0.73 and 0.74 in $Sm_{1-x}Y_xTiTaO_6$ in the radio frequency range (10^2–1.3×10^7 Hz).

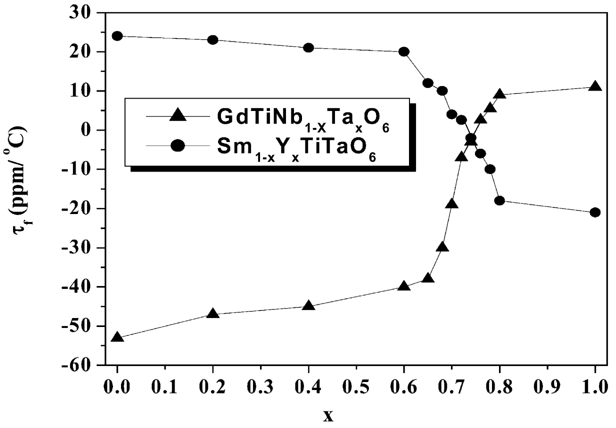

Fig. 8. Variation of the temperature coefficient of resonant frequency τ_f with composition x.

sitions $GdTiNb_{0.25}Ta_{0.75}O_6$ and $Sm_{0.27}Y_{0.73}TiTaO_6$ but it was not possible to measure their dielectric properties due to the high loss factor for these compositions.

The unloaded quality factor of these ceramics is plotted in Fig. 9 as a function of x. In $GdTiNb_{1-x}Ta_xO_6$ solid solution the $Q_u$xf of the end members are around 13,000 except near the transition region. In $Sm_{1-x}Y_xTiTaO_6$ ceramics the quality factor increases with increase in x except near the phase transition region. The very low Q factor near the phase transition region is attributed to the fact that the ceramics are porous (difficult to densify) and the atoms are in a state of re-orientation to form the new structure. A similar drop in quality factor near the aeschynite to euxenite morpotropic phase transition [23–24] transition region was observed by Surendran et al. on $RE_{1-x}RE'_xTiNbO_6$ (RE = Pr, Nd, Sm; RE′ = Gd, Dy, Y) ceramics.

It is interesting to note that the abrupt change in the microwave dielectric properties depend up on the average ionic radius of the rare earth ions in $Sm_{1-x}Y_x$ $TiTaO_6$ ceramics. The average ionic radii[31] of the solid solution phases are plotted against bulk density and unloaded quality factor (see Fig. 10). It is evident that the bulk density and quality factor reaches the minimum value when average rare earth ionic radius (IR) is 0.915 Å. Moreover it is clear from Fig. 11 that τ_f approaches zero value when the average rare earth ionic radius approaches 0.915 Å. Hence $Sm_{1-x}Y_xTiTaO_6$ ceramics will have aeschynite phase with positive τ_f when IR> 0.915 Å and vise versa. These results are in good agreement with the detailed investigation on the microwave dielectric properties of $RETiTaO_6$ made before which predicted that τ_f is minimum [22] when ionic radius of the rare earth is between 0.91Å (for $DyTiTaO_6$) and 0.92 Å (for $HoTiTaO_6$) and the border line of the aeschynite-euxenite phase transition lies for 0.91 Å <IR <0.92 Å. In other words the microwave dielectric properties of $RE_{1-x}RE'_xTiTaO_6$ ceramics can be tailored by suitably adjusting the average ionic radius of the rare earth ions which is similar to the observations made on RE_{1-x} RE'_xTiNbO_6 where the morphotropic phase transition occurs when IR = 0.945 Å.

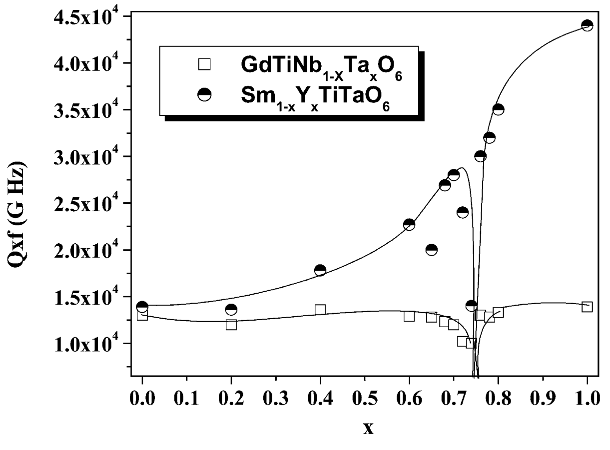

Fig. 9. Variation of the unloaded quality factor (Q_u) with composition x.

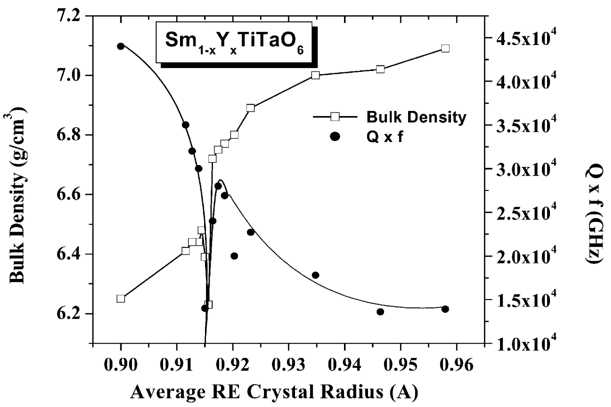

Fig. 10. Variation of bulk density and unloaded quality factor with average ionic radius of rare earths in $Sm_{1-x}Y_xTiTaO_6$.

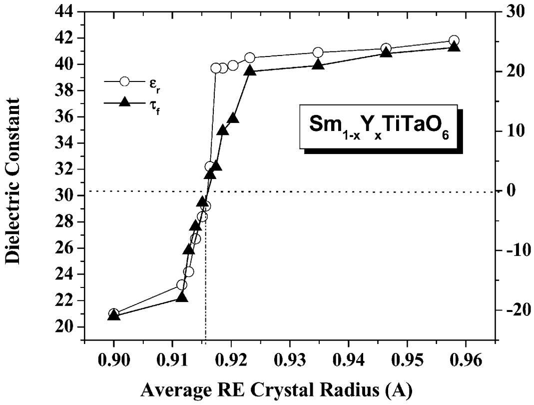

Fig. 11. Variation of τ_f and ε_r with average ionic radius of rare earths in Sm_{1-x} Y_xTiTaO_6.

4. Conclusion

Microwave dielectric ceramics based on $GdTiNb_{1-x}Ta_xO_6$ and $Sm_{1-x}Y_xTiTaO_6$ [$x = 0.0$–1.0] was prepared for different values of × using the mixed oxide route and their dielectric properties were characterized in the microwave frequency region. The dielectric properties vary linearly as function of×until a phase transition from aeschynite to euxenite occurs. The microwave dielectric properties vary abruptly near the morphotropic phase transition, which is contributed by the relative proportions of the two coexisting phases in the two-phase region. The bulk density attains minimum value for $x = 0.75$ in $GdTiNb_{1-x}Ta_xO_6$ and $x = 0.73$ in $Sm_{1-x}\,Y_xTiTaO_6$ where the τ_f changes sign. The dielectric loss factor for these solid solution compositions is unusually higher which is confirmed by the measurements at the low frequency region. The range of solid solubility of aeschynite in euxenite and vise versa depends on the average ionic radius of the rare earth ion in $RE_{1-x}RE'_xTiTaO_6$ ceramics. If the average ionic radius of the rare earths in $RE_{1-x}RE'_xTiTaO_6$ is less than 0.915 Å then the structure is euxenite with negative τ_f and when it is greater than 0.915 Å then τ_f is positive with aeschynite structure. The results indicate the possibility of developing a near zero τ_f material in the solid solution $RE_{1-x}RE'_xTiTaO_6$ by adjusting the average ionic radius of rare earth to be about 0.915 Å.

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