

Microwave dielectric properties of RETiTaO_6 (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In) ceramics

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Microwave dielectric ceramics based on RETiTaO_6 (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In) were prepared using a conventional solid-state ceramic route. The structure and microstructure of the samples were analyzed using x-ray diffraction and scanning electron microscopy techniques. The sintered samples were characterized in the microwave frequency region. The ceramics based on Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy, which crystallize in orthorhombic aeschynite structure, had a relatively high dielectric constant and positive τ_f while those based on Ho, Er, and Yb, with orthorhombic euxenite structure, had a low dielectric constant and negative τ_f . The RETiTaO_6 ceramics had a high-quality factor. The dielectric constant and unit cell volume of the ceramics increased with an increase in ionic radius of the rare-earth ions, but density decreased with it. The value of τ_f increased with an increase in RE ionic radii, and a change in the sign of τ_f occurred when the ionic radius was between 0.90 and 0.92 Å. The results indicated that the boundary of the aeschynite to euxenite morphotropic phase change lay between DyTiTaO_6 and HoTiTaO_6 . Low-loss ceramics like ErTiTaO_6 ($\epsilon_r = 20.6$, $Q_{ur}xf = 85,500$), EuTiTaO_6 ($\epsilon_r = 41.3$, $Q_{ur}xf = 59,500$), and YTiTaO_6 ($\epsilon_r = 22.1$, $Q_{ur}xf = 51,400$) are potential candidates for dielectric resonator applications.

I. INTRODUCTION

Dielectric resonators (DRs) have gained a prominent position as the key components of microwave communication systems. This is due to the capability of DRs to reduce the size of microwave components in temperature-stable filters and oscillators. The important characteristics required for a ceramic to be used for dielectric resonator applications¹ are (i) low dielectric loss, which enhances the selectivity of the low-noise oscillators and narrow-band filters with low insertion loss; (ii) high dielectric constant (ϵ_r), which facilitates miniaturization since the size of the resonator is inversely proportional to $(\epsilon_r)^{1/2}$; and (iii) low or zero temperature coefficient of resonant frequency (τ_f), which is mandatory for the temperature stability of the microwave components. A large number of ceramic dielectric materials have been developed¹⁻⁷ over the years, though there has been not even a single material that can satisfy all the

requirements. The search for new materials with an optimum balance of microwave dielectric properties is one of the most challenging problems in material science.

It is interesting to note that most of the useful microwave dielectric ceramic materials developed in recent years are complex oxides of titanates, tantalates, or niobates. However microwave ceramics involving both titanium and tantalum/niobium are quite few in number. Many researchers investigated the structural properties of ceramics of the type AB_2O_6 .⁸⁻¹⁰ Of these, $\text{A}^{3+}\text{B}^{4+}\text{C}^{5+}\text{O}_6$ constitutes a special group whose single-phase occurrence was first substantiated by Kazantsev *et al.* in 1974.¹¹ They established the optimum conditions of formation of double tantalates of rare-earth elements with titanium based on the formula LnTiTaO_6 , where Ln is a lanthanide. In the same investigation it was shown that rare-earth titanium tantalate compounds with a rare-earth atomic number in the range of 57–66 have orthorhombic aeschynite symmetry, whereas compounds with a rare-earth atomic number of 67–71 have orthorhombic euxenite symmetry. Later Holcombe^{12,13} studied the

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crystal structure of ternary oxides such as AlTiTaO₆ and YTiTaO₆ since these compounds possess a unique low thermal expansion coefficient and high melting point. In 1987 Maeda *et al.*¹⁴ suggested the possibility of using tantalates and niobates related to TiO₂ such as MTi-(Ta,Nb)O₆ (M = Al, Y, and Dy) for microwave frequency applications. He suggested that the possible high dielectric constant and high quality factor might be due to the contribution from the TiO₆ octahedron. Very recently, Sebastian *et al.* reported the microwave dielectric properties of RETiNbO₆ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, and Yb) ceramics.¹⁵ They found that in a rare-earth titanium niobate system, members of the aeschynite group (compounds with the atomic number of the rare-earth ions in the range of 57–63 in the periodic table) have a positive τ_f with a high dielectric constant, whereas euxenites (compounds with the atomic number of the rare-earth ions in the range of 64–71) have a negative τ_f with a lower dielectric constant. They also tailored the microwave dielectric properties of RETiNbO₆^{16,17} by making solid-solution phases with materials having positive and negative τ_f in an effort to tune the value of τ_f to a minimum. Recently Solomon reported that RETiTaO₆ ceramics could be used as a promising material for DR applications because of their higher unloaded quality factor over RETiNbO₆ ceramics at the microwave frequency range.¹⁸ Though the synthesis, characterization, and properties of rare-earth titanium niobates have been investigated in detail, a similar study on rare-earth titanium tantalates has not been attempted before. In this paper we report the structure and microwave dielectric properties of RETiTaO₆ [RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In] ceramics.

II. EXPERIMENTAL

The RETiTaO₆ ceramics were prepared by the conventional solid-state ceramic route. High-purity (>99%) oxides of rare earth, titanium, and tantalum were used as the starting materials. (Highly hygroscopic rare-earth oxides like La₂O₃ and Ho₂O₃ were heated before weighing at a temperature of 1100 °C for 5 h to remove moisture that could alter the stoichiometry of rare-earth ions in the reaction mixture). The chemicals were weighed according to the stoichiometric compositions and were ball milled using a polyethylene mill bottle with zirconia balls in distilled water for 48 h. The slurry was dried at 100 °C in a hot air oven and was calcined at 1250 °C for 8 h with intermediate grinding. AlTiTaO₆ and InTiTaO₆ were calcined at a lower temperature of 1200 °C. The slurry was then ground for several hours in an agate mortar. Five weight percent poly vinyl alcohol (PVA) was added as the binder and the material was pressed into cylindrical disks of about 14-mm diameter and 6–8-mm thickness in a tungsten carbide die under a pressure of

about 200 MPa. These compacts were fired at a rate of 5 °C/min up to 600 °C and soaked at 600 °C for 1 h to expel the binder before they were sintered in the temperature range of 1500–1625 °C for 4 h in air at a heating rate of 10 °C/h. The sintering temperature varied from rare earth to rare earth, and the temperature corresponding to the best dielectric properties was taken as the optimum sintering temperature. The well-polished ceramic pellets were used for microwave measurements. The bulk density of the sintered samples was measured using the Archimedes method. The powdered samples were used for analyzing the x-ray diffraction (XRD) patterns using Cu K α radiation (Rigaku-Dmax 1C, Tokyo, Japan). The sintered samples were thermally etched for 30 min at a temperature about 50 °C below the sintering temperature, and the surface morphology was studied using a scanning electron microscope (JOEL-JSM 5600 LV, Tokyo, Japan).

The dielectric properties ϵ_r and τ_f of the materials were measured in the microwave frequency range using a network analyzer HP 8510C (Hewlett-Packard, Palo Alto, CA). The dielectric permittivity ϵ_r was measured by the post resonator method of Hakki and Coleman¹⁹ using the TE₀₁₈ mode of resonance coupled through E-field probes as described by Courtney.²⁰ The unloaded quality factor Q_u of the resonance was determined using the cavity method.²¹ The coefficient of thermal variation of resonant frequency (τ_f) was measured by noting the temperature variation of the resonant frequency of TE₀₁₈ mode in the reflection configuration over a temperature range of 25–75 °C when the sample was kept in the end-shortened position.

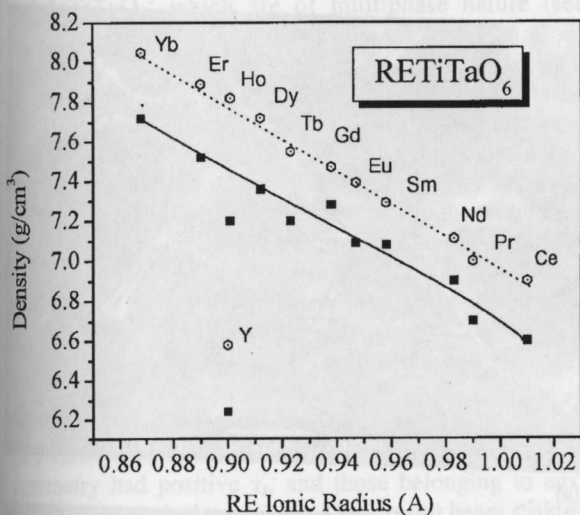
III. RESULTS AND DISCUSSION

RETiTaO₆ was sintered into dense ceramics. The densities of the ceramics are given in Table I. Most of the RETiTaO₆ ceramics were sintered to above 95% of their theoretical densities. Figure 1 represents the variation of theoretical density and experimental density with ionic radius²² of the rare-earth ions in RETiTaO₆. The density of the ceramics decreased with an increase in the ionic radius of the rare earth. The theoretical, as well as experimental, density decreased with an increase in the ionic radius because of two contributing factors: (i) the replacement of the rare-earth ion with a lighter one and (ii) the increase of the unit cell volume. The density of YTiTaO₆ is lower than that of the rest of the rare-earth titanium tantalates. This is expected since yttrium is lighter than the rest of the rare-earth elements. The density of the LnTiTaO₆ ceramics is also low because of their multiphase nature [see Fig. 4(b)].

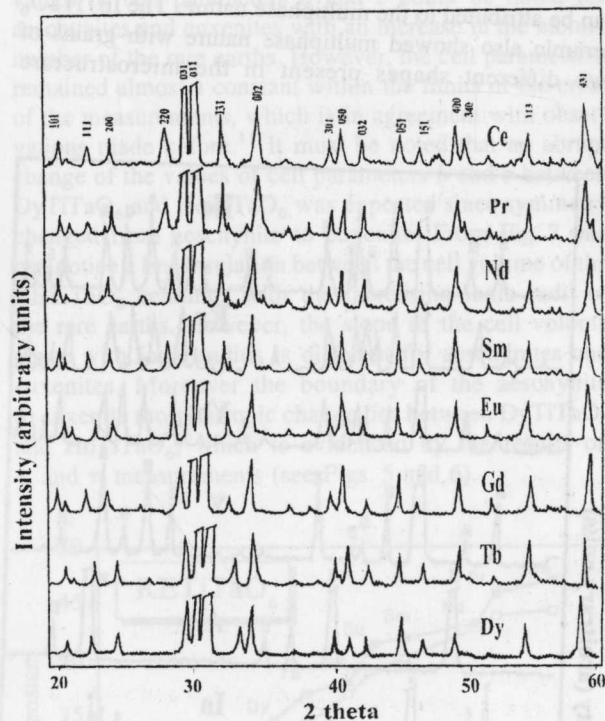
Figure 2 shows the XRD patterns recorded from powdered RETiTaO₆ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) ceramics. It is evident from the figure that the XRD

TABLE I. Microwave dielectric properties of RETiTaO₆.

RE ion	Theoretical density (g/cm ³)	% Densification	ϵ_r	τ_f (ppm/°C)	$Q_u \times f$ (GHz)	Sintering temperature (°C)	Lattice parameters (Å)		
							<i>a</i>	<i>b</i>	<i>c</i>
La	6.81 ^a	89	24.4	-39	45300	1530	5.45 ^a	10.96 ^a	7.56 ^a
Ce	6.9	96	46.0	+41	33300	1540	5.399	10.970	7.536
Pr	7.0	97	45.8	+33	32300	1500	5.380	10.959	7.501
Nd	7.11	95	43.1	+30	26400	1550	5.351	10.968	7.530
Sm	7.29	97	41.8	+24	11600	1500	5.299	10.970	7.500
Eu	7.39	96	41.3	+19	59500	1525	5.291	10.969	7.420
Gd	7.47	98	37.9	+11	12900	1540	5.269	10.980	7.410
Tb	7.55	94	36.8	+10	32300	1525	5.242	10.979	7.390
Dy	7.72	95	34.6	+7	40100	1500	5.211	10.979	7.380
Ho	7.82	90	23.1	-8	46900	1550	5.529	14.559	5.160
Y	6.58	98	22.1	-20	51400	1625	5.501	14.571	5.179
Er	7.89	96	20.6	-29	85500	1560	5.520	14.559	5.160
Yb	8.05	94	19.3	-41	31800	1560	5.501	14.540	5.129
In	24.3	+39	15400	1525
Al	6.28	98	28.1	+20	10000	1575	4.579	4.578	4.943

^aData given in Ref. 11.FIG. 1. Variation of density, theoretical density (dotted line), and experimental density (solid line), with ionic radius of the rare earth in RETiTaO₆.

patterns of CeTiTaO₆, PrTiTaO₆, NdTiTaO₆, SmTiTaO₆, EuTiTaO₆, GdTiTaO₆, TbTiTaO₆, and DyTiTaO₆ are similar and are in agreement with ICDD File No. 28-1289 for TbTiTaO₆.²³ The XRD patterns of HoTiTaO₆, ErTiTaO₆, and YbTiTaO₆ ceramics are similar (see Fig. 3) and are comparable with ICDD File Card No. 27-1157 for HoTiTaO₆.²⁴ Like in RETiNbO₆ ceramics, the members of RETiTaO₆ system can exist in two orthorhombic structural forms such as aeschynites and euxenites, which is in agreement with observations made before.¹¹ The powder diffraction pattern of YTiTaO₆ is identical to ICDD File Card No. 32-1452.²⁵ However it is different from the XRD pattern of the rest of the euxenite ceramics in the RETiTaO₆ system though the

FIG. 2. Powder XRD patterns of aeschynites in RETiTaO₆ (CeTiTaO₆, PrTiTaO₆, NdTiTaO₆, SmTiTaO₆, EuTiTaO₆, GdTiTaO₆, TbTiTaO₆, and DyTiTaO₆).

microwave dielectric properties of this DR show striking similarity with euxenites. The crystal structure of LaTiTaO₆ has already been reported as orthorhombic with aeschynite symmetry.¹¹ However, the XRD patterns obtained in our experiment were different from the rest of the aeschynites, indicating the nature of multiphase with peaks of two distinct phases such as La₂Ti₂O₇ and Ta₂O₅

(Fig. 3). The XRD pattern of InTiTaO₆ also seemed to be different from the rest of the ceramics in the RETiTaO₆ system. In InTiTaO₆ peaks of multiphases, such as In₂TiO₅ and InTaO₄, are also visible in the XRD pattern (see Fig. 3). The presence of multiphase in LaTiTaO₆ and InTiTaO₆ ceramics was confirmed through scanning electron microscopy (SEM). The XRD pattern of AlTiTaO₆ (ICDD File No. 32-28)²⁶ appears to represent a different structural type in the ABCO₆ compounds. Since the material has the tetragonal cassiterite structure it could be considered as a solid solution because TiO₂ and Ta₂O₅ have the same tetragonal structure and Al³⁺ could be considered as substituting into this structure.¹³

Figure 4(a) shows the SEM micrograph of the LaTiTaO₆ ceramic sintered at 1530 °C/4 h. Two distinct phases are visible in this micrograph, and one of the phases started melting at 1530 °C. Some of the grains also show microcracks. The poor densification (89%) and anomalous microwave dielectric properties of LaTiTaO₆ ceramics can be attributed to the multiphase nature. The InTiTaO₆ ceramic also showed multiphase nature with grains of two different shapes present in the microstructure

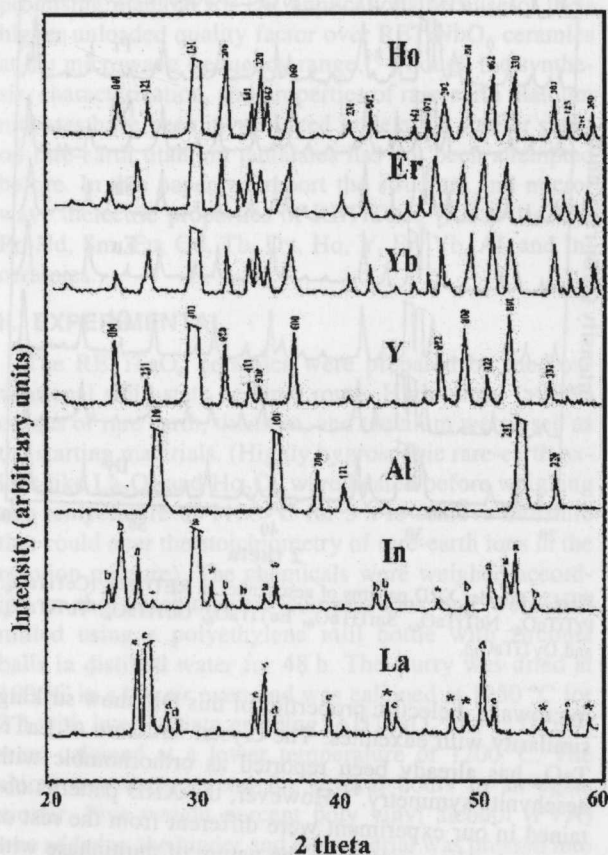


FIG. 3. Powder XRD patterns of HoTiTaO₆, ErTiTaO₆, YbTiTaO₆, YTiTaO₆, AlTiTaO₆, InTiTaO₆, and LaTiTaO₆.

[Fig. 4(b)]. The two phases are La₂Ti₂O₇ and Ta₂O₅, whose presence was substantiated by powder XRD analysis.

It is well known that extrinsic factors like porosity considerably affect the measured dielectric constant of a ceramic material. Penn *et al.* suggested a correction for the dielectric constant of a material if the percentage densification of the sintered bodies is known.²⁷

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

where ϵ' is the dielectric constant of the composite, which contains a porosity P , and ϵ_m is the actual dielectric constant of the dielectric. Figure 5 gives the variation of ϵ_r (experimental) and ϵ_r (corrected for porosity) with the ionic radius of the rare earth in RETiTaO₆. The dielectric constant of the ceramics increased with an increase of ionic radii of the rare earths. It is evident that

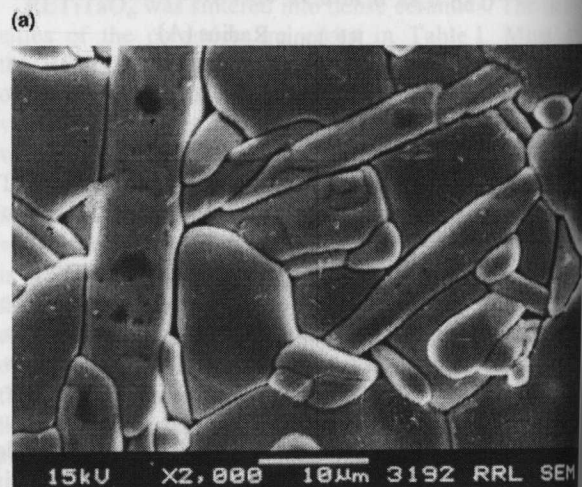
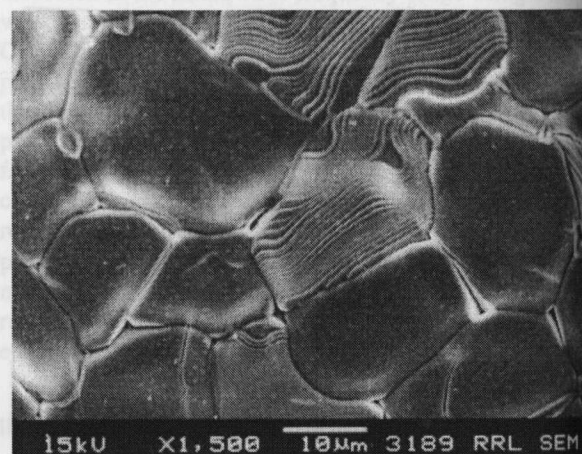


FIG. 4. SEM micrograph of (a) LaTiTaO₆ sintered at 1530 °C and (b) InTiTaO₆ sintered at 1525 °C for 4 h.

dielectric constants of aeschynite-type RETiTaO₆ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) were comparatively high, varying from 46.9 to 34.6, while those of the euxenite type ceramics, such as HoTiTaO₆, YTiTaO₆, ErTiTaO₆ and YbTiTaO₆, were low, varying from 23 to 21. These results agreed with those of RETiNbO₆ in which aeschynites (CeTiNbO₆, PrTiNbO₆, NdTiNbO₆, SmTiTaO₆, and EuTiTaO₆) had high dielectric constants, whereas euxenites (GdTiNbO₆, TbTiNbO₆, DyTiNbO₆, YTiNbO₆, and YbTiNbO₆) had relatively low dielectric constants. According to the Claussius–Massotti (CM) equation, the dielectric constant of a material depends on two parameters: volume of the unit cell and the total ionic polarizability²⁸ of the cations and anions constituting the chemical formula of the material. Since the total ionic polarizability and cell volume increased from YbTiTaO₆ to CeTiTaO₆, the monotonous increase of dielectric constant with ionic radius closely agreed with theory. The microwave ceramics LaTiTaO₆ and InTiTaO₆, which are of multiphase nature (see Fig. 2), have dielectric constants of 24.4 and 24.3, respectively. The dielectric constant of AlTiTaO₆ is 29.4 and has a tetragonal symmetry. It must be noted that in 1987 Maeda *et al.* attempted to measure the microwave dielectric properties of a few rare-earth titanium tantalate ceramics like AlTiTaO₆, NdTiTaO₆, and YTiTaO₆ in an effort to search for new DR materials with coulombite structure. However, the dielectric constants they measured were lower than what is reported in this paper, which may be due to the high percentage of porosity (>20%) contained in their ceramic samples.

The temperature coefficient of resonant frequency was plotted against ionic radius of the rare earths in RETiTaO₆ (see Fig. 6 and Table I). It was evident that rare-earth titanium tantalates belonging to aeschynite symmetry had positive τ_f , and those belonging to euxenite symmetry had negative τ_f . This result bears striking

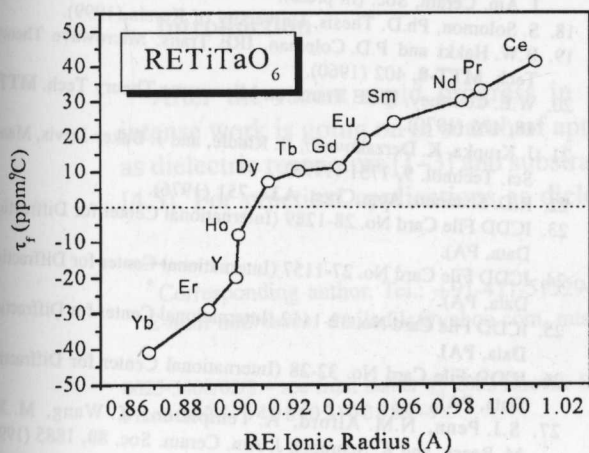


FIG. 5. Variation of the dielectric constant with ionic radius of the rare earth in RETiTaO₆.

similarity with the niobium counterparts.¹⁵ It is interesting to note that the ionic radius of ceramics in RETiTaO₆ system with low τ_f (DyTiTaO₆ and HoTiTaO₆) was between 0.9 and 0.92 Å. The results of τ_f measurements in RETiTaO₆ indicated that the aeschynite–euxenite phase transition boundary lies between DyTiTaO₆ and HoTiTaO₆. In other words, one can tailor the value of τ_f to a minimum by making a solid solution between aeschynites and euxenites to bring down the average ionic radii of the rare earths to between 0.9 and 0.92 Å, similar to rare-earth titanium niobates.¹⁷ The values of τ_f of the multiphase compounds LaTiTaO₆ and InTiTaO₆ were -38 and $+39$ ppm/°C, respectively, while that of tetragonal AlTiTaO₆ was $+20$ ppm/°C. It must be noted that a number of RETiTaO₆ ceramics had relatively lower τ_f values, which could be tuned by proper substitution and doping.

On comparison of the lattice parameters of RETiTaO₆ ceramics (see Table I), a monotonic decrease of the values of cell parameters a and c could be noted for aeschynites and euxenites with an increase in the atomic number of the rare earths. However, the cell parameter b remained almost a constant within the limits of the error of the measurements, which is in agreement with observations made before.¹¹ It must be noted that an abrupt change of the values of cell parameters b and c between DyTiTaO₆ and HoTiTaO₆ was expected since symmetry changed from aeschynite to euxenite. From Fig. 7 one can notice a linear relation between the cell volume of the RETiTaO₆ ceramics with the increasing ionic radii of the rare earths. However, the slope of the cell volume curve with ionic radius is different for aeschynites and euxenites. Moreover the boundary of the aeschynite to euxenite morphotropic change lies between DyTiTaO₆ and HoTiTaO₆, which is evidenced by the results on ϵ_r and τ_f measurements (see Figs. 5 and 6).

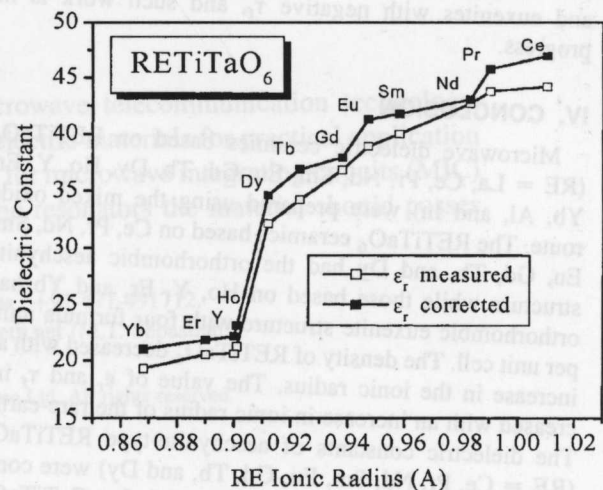


FIG. 6. Variation of τ_f with ionic radius of the rare earth in RETiTaO₆.

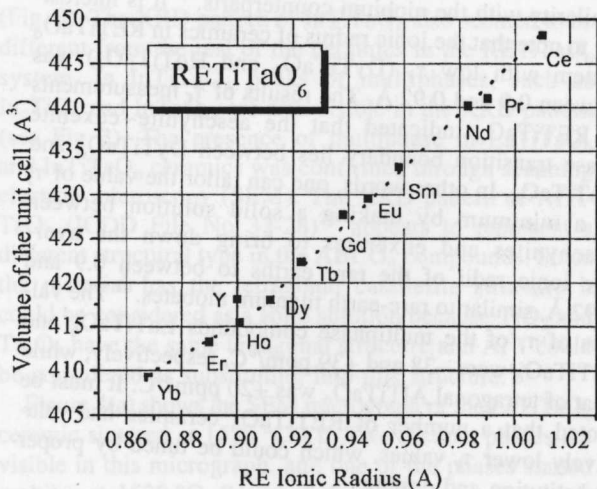


FIG. 7. Variation of the volume of the unit cell with ionic radius of the rare earth in RETiTaO₆.

From Table I it is clear that most of these dielectric resonators have high dielectric constants and high reloaded Q factors (Q_u) compared to their niobium counterparts. It is observed that low-loss ceramics like ErTiTaO₆ ($\epsilon_r = 20.6$, $Q_u \times f = 85,500$), EuTiTaO₆ ($\epsilon_r = 41.3$, $Q_u \times f = 59,500$) and YTiTaO₆ ($\epsilon_r = 22.1$, $Q_u \times f = 51,400$) can be used as potential candidates for DR applications. The high dielectric constant materials may also be useful in the semiconductor industry as suitable substrates to silicon dioxide in memory devices²⁹ or as substrates for microwave integrated circuits. The material LaTiTaO₆ proved to be a low loss ceramic with a high quality factor ($Q_u \times f = 46,300$) in spite of it being of multiphase nature. The quality factors of AlTiTaO₆ and InTiTaO₆ are relatively low as seen from Table I. It may be possible to tailor the τ_f and ϵ_r by making a solid-solution phase between the aeschynites with positive τ_f and euxenites with negative τ_f , and such work is in progress.

IV. CONCLUSION

Microwave dielectric ceramics based on RETiTaO₆ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al, and In) were prepared using the mixed oxide route. The RETiTaO₆ ceramics based on Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy had the orthorhombic aeschynite structure while those based on Ho, Y, Er, and Yb had orthorhombic euxenite structure with four formula units per unit cell. The density of RETiTaO₆ decreased with an increase in the ionic radius. The value of ϵ_r and τ_f increased with an increase in ionic radius of the rare-earth. The dielectric constants of aeschynite-type RETiTaO₆ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) were comparatively high and varied from 46.9 for CeTiTaO₆ to 34.6 for DyTiTaO₆, while those of euxenite type

ceramics, such as HoTiTaO₆, YTiTaO₆, ErTiTaO₆, and YbTiTaO₆, were low and varied from 23 to 21. Rare-earth titanium tantalates belonging to aeschynite symmetry had positive τ_f , and those belonging to euxenite structure had negative τ_f . In RETiTaO₆ system τ_f was low when the ionic radius of the rare-earth ion lay between 0.9 and 0.92 Å.

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