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Fabrication and characterization of xPrTiTaO$_6$(1 − x)YTiNbO$_6$ microwave ceramic composites

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ABSTRACT

The xPrTiTaO$_6$(1 − x)YTiNbO$_6$ microwave dielectric ceramic composites are fabricated through the solid state ceramic route. The compositions are calcined in the temperature range 1200–1260 °C and sintered in the range 1350–1450 °C. The structure is analyzed using X-ray diffraction technique and confirmed using Raman spectroscopy. Surface morphology is studied using scanning electron microscopy. The variation of bulk density, quality factor ($Q_u$xf), temperature coefficient of resonant frequency (τ_f) and dielectric constant (ε_r) are correlated. Most of the samples have high ε_r, high $Q_u$xf and low τ_f and hence are suitable for dielectric resonator applications.

1. Introduction

At present, the science and technology of materials with tailor-made characteristics is in such an advanced state that one can control the parameters that influence the desired properties. Development of new materials with the most suitable dielectric properties for specific applications is a challenging problem. One among them is the resonator that plays a key role in the field of microwave communication. At the resonant frequency, electric and magnetic energies must be stored equally inside the dielectric resonator so that electromagnetic waves can be transmitted with minimal loss. The resonator bandwidth or the dielectric loss is inversely proportional to the quality factor. Miniaturization can be achieved by producing dielectric resonators with high dielectric constant. Low or zero temperature coefficient of resonant frequency (τ_f) is important for the temperature stability of the microwave components.

According to Kazantsev et al. [1] rare-earth titanium tantalate compounds with the rare-earth atomic number in the range 57–66 have orthorhombic aeschynite symmetry with space group *Pnma*, and that with atomic number in the range 67–71 have orthorhombic euxenite symmetry with space group *Pbcn*. In 1987 Maeda et al. [2] suggested the possibility of using tantalates and niobates related to TiO$_2$ such as MTi (Ta, Nb) O$_6$ (M = Al, Y and Dy) for microwave frequency applications. They suggested that the possible high dielectric constant and high quality factor might be due to the contribution of TiO$_6$ octahedron. Sebastian et al. [3] reported the microwave dielectric properties of RETiNbO$_6$ (Re = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y and Yb) ceramics. They found that, in rare-earth titanium niobate system, members of the aeschynite group have positive τ_f with high dielectric constant, whereas euxenites have negative τ_f with low dielectric constant. Sam Solomon et al. [4] reported that the solid solution phases between the aeschynite and the euxenite groups possess intermediate dielectric constant and τ_f values. Reaney and Iddles [5] in 2006 mentioned the creation of a solid solution or composite of two materials, each having opposite signs of τ_f. Recently Padma Kumar et al. [6] have reported the solid solution formation of Nd–Y titanium tantalate ceramics. They have also reported the doping effect of MoO$_3$ and WO$_3$ in LnTiTaO$_6$ system [7]. Solomon et al. [8] have reported the partial substitution of Zr in the Ti site of these materials. In this paper we report the synthesis, characterization and microwave dielectric properties of praseodymium titanium tantalate and yttrium titanium niobate mixtures for the first time.

2. Experimental

The xPrTiTaO$_6$(1 − x)YTiNbO$_6$ ceramics were prepared through the conventional solid state ceramic route. High purity (>99%) oxides of Pr, Y, Ti, Ta and Nb were weighed in stoichiometric ratio. The weighed stoichiometric compositions were ball-milled in polyethylene mill bottle with zirconia balls and acetone for 2 h. The slurry was dried and calcined at 1200 °C for PrTiTaO$_6$ (PTT) and 1260 °C for YTiNbO$_6$ (YTN) for 4 h. The calcined slurry was ground for about 2 h in an agate mortar. It was again ball-milled in acetone medium for about 3 h. For x = 1, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.0, the above calcined powder of PTT and YTN was weighed and ball-milled for 6 h in acetone medium. Again the slurry was dried out. Five weight percent poly

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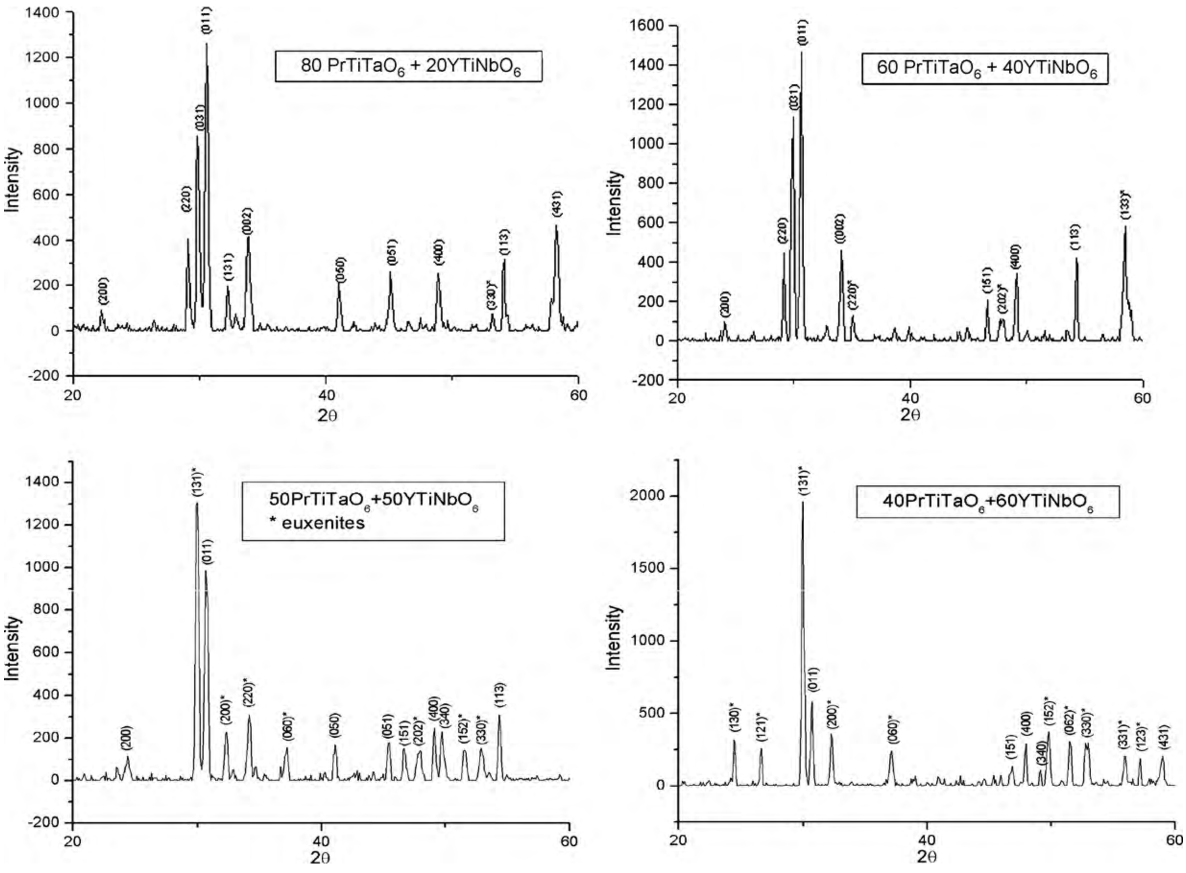

Fig. 1. XRD patterns of selected samples.

vinyl alcohol (PVA) was added as binder. The material was pressed into cylindrical disks of about 14 mm diameter and 8–9 mm thickness using hydraulic press under a pressure of about 150 MPa. These compacts were fired at a rate of 5 °C/min up to 600 °C and soaked at 600 °C for 30 min to expel the binder before they were sintered in the temperature range of 1350–1450 °C for 4 h. The bulk density of the sintered pellets was measured using Archimedes method. The powdered samples were used for XRD analysis (Diffractometer system XPERT-PRO). Surface morphological study of selected compositions was done (JEOL JSM 5610 LV). The well polished ceramic pellets were used for microwave dielectric measurements using cavity resonator method with the network analyzer (Agilent 8753 ET). The temperature coefficient of resonant frequency (τ_f) was also measured over a temperature range of 20–70 °C. FT-Raman spectra of selected samples were recorded at room temperature over the wavenumber range 50–1000 cm^{-1} using Bruker RFS 100/S spectrometer at a power level of 50 mW and at a resolution of 4 cm^{-1}. The samples were excited with an Nd:YAG laser lasing at 1064 nm and the scattered radiations were detected using a standard Ge detector.

3. Results and discussion

Fig. 1 shows the XRD patterns of the sintered xPTT$(1-x)$YTN composites where x = 1.0, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.0. All the major peaks are indexed on the basis of the reported papers [3,9]. The XRD pattern of the composition containing 80% of PTT (80PTT) shows more reflections of aeschynite structure while that of 40PTT composition shows more reflections of euxenite structure. We can see a change in symmetry from aeschynite to euxenite in between these two compositions. It can be seen that for 60PTT there is a slight domination of aeschynite reflections while euxenite reflections are dominant for 50PTT. The peaks marked as (*) are the reflections of euxenite structure.

Fig. 2 shows the SEM micrograph of 50PTT composition sintered at 1380 °C/4 h. This picture reveals that the sample is well sintered with minimum porosity. Elongated and equiaxed grains are observed in the micrograph. Oishi et al. [10] have reported that aeschynite structure has elongated grains whereas euxenite structure has equiaxed grains.

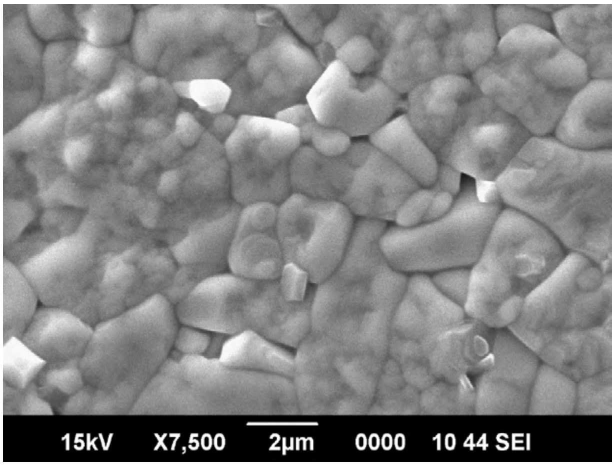

Fig. 2. SEM of 50PTT composition.

According to Harrop [11], compounds with low ε_r in general exhibit low τ_f and vice versa. A graph plotted between ε_r and τ_f is given in Fig. 3. An approximate linear variation can be seen in the present study also, indicating the linearity between ε_r and τ_f. The quality factor ($Q_u$xf), resonating frequency (*f*), temperature coefficient of resonant frequency (τ_f) and dielectric constant (ε_r) are tabulated (Table 1). Dielectric constant varies from 20.20 to 37.50 and τ_f varies from −45.07 to +42.81 ppm/°C. For 50–50 composition sintered at 1380 °C, the τ_f is minimum, i.e., −1.9 ppm/°C and ε_r is 33.78. There is a possibility of nonlinear variation in dielec-

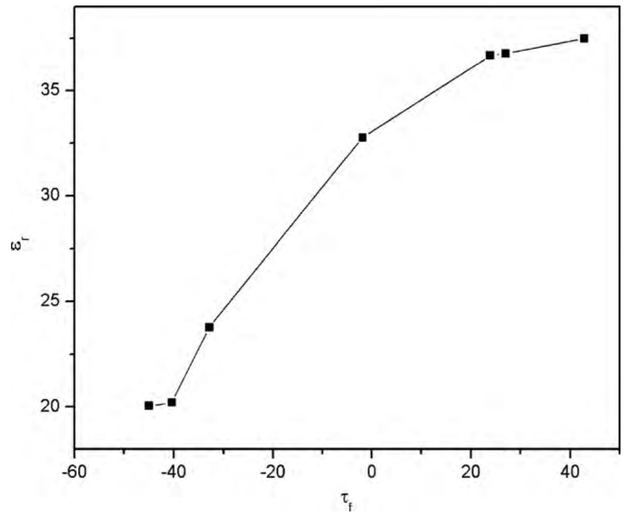

Fig. 3. Variation of ε_r with τ_f.

Table 1
Dielectric properties sintered in the range 1380–1410 °C.

Composition	Qxf (GHz)	ε_r	τ_f (ppm/°C)	f (GHz)	Sintering temperature(°C)
100PTT + 0YTN	17,800	37.5	42.81	4.05	1380
80PTT + 20YTN	9650	36.78	27.03	3.95	1380
60PTT + 40YTN	12,400	36.69	23.89	3.87	1380
50PTT + 50YTN	13,500	33.78	−1.9	4.22	1380
40PTT + 60YTN	18,000	23.79	−32.86	4.84	1380
20PTT + 80YTN	24,000	20.20	−48.41	5.2	1380
0PTT + 100YTN	22,000	20.43	−45.07	5.1	1410

tric constant and τ_f when the sample is in the region of change of symmetry from aeschynite to euxenite [12]. Hence the composite ceramic 50PTT of this series is the most suitable material as a dielectric resonator.

Average theoretical density was calculated by taking the sum of the product of percentage composition and the theoretical densities of tantalates and niobates. Fig. 4 portrays the comparable similarity of average theoretical density and experimental density with respect to the percentage composition of PTT (x). The densities increase with the increase in x. The variation of ε_r and τ_f with respect to the average theoretical and experimental densities is given in Fig. 5(a) and (b), respectively. Both ε_r and τ_f increase with the increase in densities. The graphs for experimental and average theoretical densities are similar and hence establishing the authenticity and reproducibility of the work.

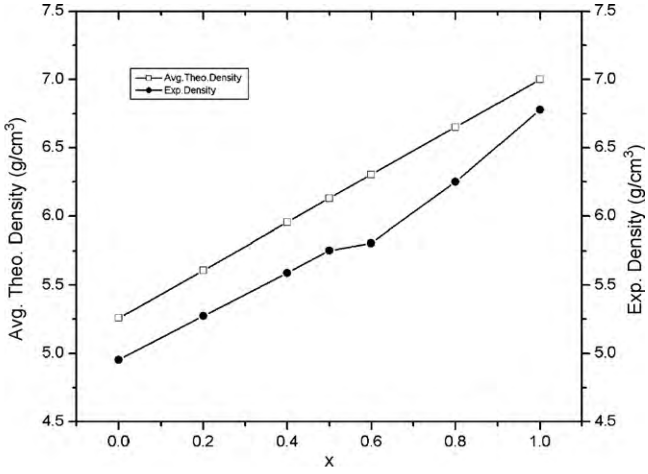

Fig. 4. Variation of average theoretical density and experimental density with x.

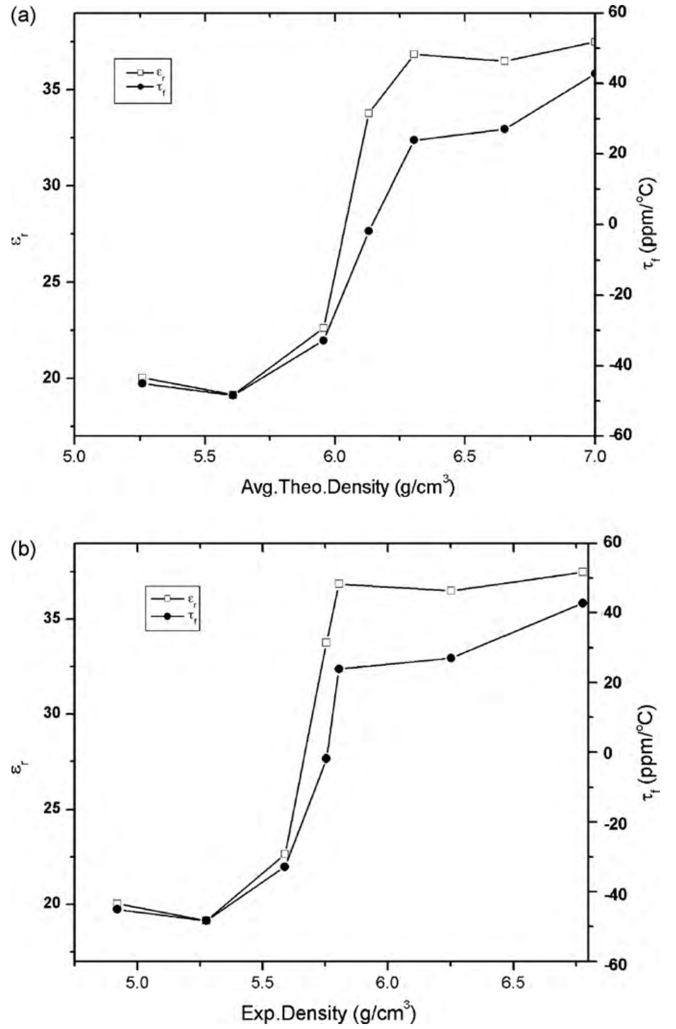

Fig. 5. (a) Variation of ε_r and τ_f with average theoretical density. (b) Variation of ε_r and τ_f with experimental density.

The Raman spectra of the samples with x = 0.4, 0.5, 0.6 and 0.8 are given in Fig. 6. The prominent peaks and their assignments are given in Table 2. Paschoal et al. [13] have reported the Raman scattering study of the microwave dielectric system RETiTaO$_6$ for 15 different rare earths. They have clearly differentiated aeschynite and euxenite structures based on the characteristic Raman bands. On comparing the measurements made in the present study with that already reported [13] it is found that the spectrum of 80PTT is exactly similar to that of PrTiTaO$_6$ which has aeschynite structure and the spectrum of 40PTT is almost similar to YTiTaO$_6$ which has euxenite structure. The spectra of 60PTT and 50PTT show both the phases in them. However, the characteristic bands show that the prominent phase is aeschynite in the former and euxenite in the latter. The XRD and dielectric measurements are in good agreement with this result. The temperature coefficient of resonant frequency, τ_f, shifts to negative values as the euxenite structure starts dominating. The three Raman active modes, namely A_{1g}, E_g and F_{2g} modes of Ta/NbO$_6$ octahedron having O_h symmetry are observed as very strong bands around 860, 671 and 315 cm^{-1}, respectively. The two IR active F_{1u} vibrations are observed as less intense bands in the range 493–372 cm^{-1} and 854–857 cm^{-1}. In the present study $\nu_1 A_{1g}$ mode, the characteristic Raman band with highest band number, is observed at 863 and 867 cm^{-1} in the case of 80PTT and 60PTT, respectively and at 854 and 855 $\mathrm{cm^{-1}}$ in the case of 50PTT and 40PTT, respectively in accordance with the earlier reports [13,14]. This confirms the prominence of aeschynite structure in 80PTT and 60PTT and the prominence of euxenite structure in the other two. This is supported by the observation that the ν_5F_{2g} mode has shifted to higher wave number side with the onset of euxenite phase on to the aeschynite structure. The multiplicity of the lattice vibrations increases towards the euxenite structure. All the peaks below 200 $\mathrm{cm^{-1}}$ can be associated with the lattice modes. The isolated modes below 90 $\mathrm{cm^{-1}}$ can be associated with the octahedral displacements [13].

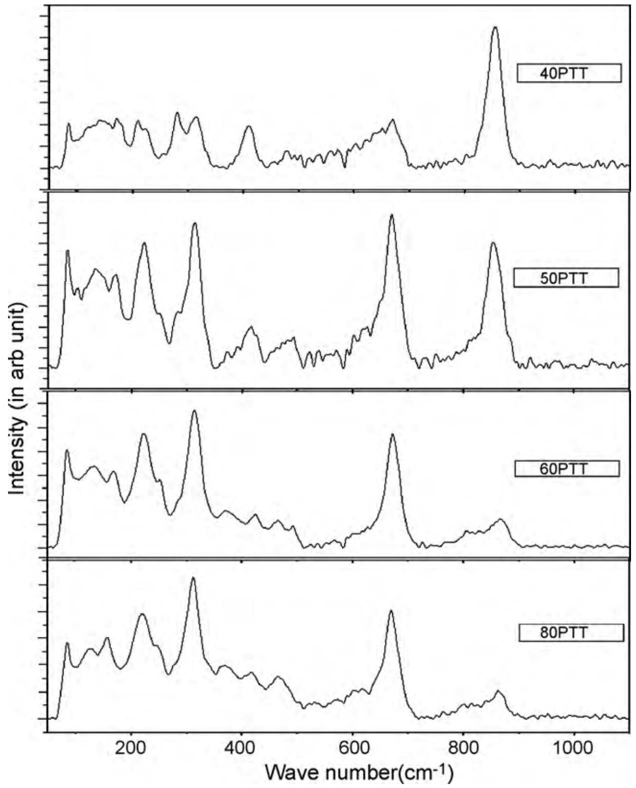

Fig. 6. Raman spectra of selected samples.

Table 2
Prominent Raman peaks and characteristic modes.

PTT80	PTT60	PTT50	PTT40	modes
863 m	867 m	854 vs	855 vvs	ν_1A_{1g}
842 w				
	815 w	812 w		
	805 w		804 vw	
670 vs	672 vs	671 vvs	670 vs	ν_1E_g
	627 w	628 m		
618 w		620 m		
604 w		604 m		
	493	492 m	480 w	ν_3F_{1u}
466 m	466 m			
420 m	426 m	422 s		
		414 m	410 s	
372 m	372 m	393 w		ν_4F_{1u}
		374 w		
312 vvs	315 vvs	315 vvs	315 vs	ν_5F_{2g}
		284 m	280 vs	
244 m	252 s	250 s		ν_6F_{2u}
220 vs	223 vs	223 vs	222 m	
			209 s	
156 m	169 s	171 s	171 s	Lattice modes
			149 m	
	134 s	134 s	140 m	
		117 w	128 m	
		104 w	117 m	
85 m	86 vs	85 vs	86 m	Octahedral displacements

Relative intensities: v, very; s, strong; m, medium; w, weak.

4. Conclusions

The $x\mathrm{PrTiTaO_6}(1-x)\mathrm{YTiNbO_6}$ ceramics were prepared through the solid state ceramic route for $x = 1$, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.0. The compositions were calcined at 1200 and 1260 °C and sintered in the range 1350–1450 °C. Structural analysis of the materials was done using XRD and Raman spectroscopy. Surface morphological study was done by SEM analysis. Microwave dielectric properties were measured using cavity resonator method. The composition with $x = 0.5$ of this series with high quality factor, high dielectric constant and low τ_f is the most suitable material for dielectric resonator applications.

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