Synthesis of low loss, thermally stable Ce$_x$Y$_{1-x}$TiTaO$_6$ microwave ceramics

H. Padma Kumar$^a$, Annamma John$^a$, C. Vijayakumar$^b$, J.K. Thomas$^c$, Manoj Raama Varma$^d$, Sam Solomon$^a,*$

$^a$Dielectric Materials Research Laboratory, Department of Physics, St. John’s College, Anchal, Kollam District, Kerala 691306, India
$^b$Electronic Materials Research Laboratory, Department of Physics, Mar Ivanios College, Nalanchira, Thiruvananthapuram, Kerala 695015, India
$^c$National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram, Kerala 695015, India

**Abstract**

Ce$_x$Y$_{1-x}$TiTaO$_6$ ceramics were prepared through the solid-state ceramic route. The materials were sintered in the range 1520–1580 °C. The structure of the system was analyzed by X-ray diffraction and Raman spectroscopic methods. The cell parameters of solid solutions were calculated using the least square method. The microstructure was analyzed using scanning electron microscopy. The dielectric constant ($\varepsilon_r$), temperature coefficient of resonant frequency ($\tau_f$), and the unloaded quality factor ($Q_u$) were measured in the microwave frequency region using cavity resonator method. The dielectric constant increases with higher concentrations of Ce in the solid solutions. Nearly zero temperature coefficient of resonant frequency ($\tau_f$) was obtained for Ce$_{0.24}$Y$_{0.76}$TiTaO$_6$. The samples are of high quality factor and are useful electronic materials for microwave applications.

**Keywords:**
A. Ceramics  
A. Electronic materials  
D. Dielectric properties  
D. Microstructure

1. Introduction

Ceramic dielectric resonators (DRs) find wide range of applications in the field of microwave communication systems [1]. Commercial DRs must combine three desirable properties such as dielectric constant ($\varepsilon_r > 25$), quality factor ($Q > 2000$), and temperature coefficient of resonant frequency ($\tau_f < \pm 20$ ppm/°C) [2]. The dielectric constant ($\varepsilon_r$) is related to the resonant frequency ($f_0$) according to the relation $f_0 = c/\varepsilon_r D^2$, where $c$ is the velocity of light in vacuum and $D$ is the diameter of the DR which means as the dielectric constant of the resonator material increases, the size of the resonator can be decreased maintaining the same resonant frequency. The quality factor $Q$ is determined as the resonant frequency divided by the bandwidth $\Delta f$, measured at 3 dB below the maximum height at resonance, which means that $Q$ is a measure of selectivity of a resonator at a given frequency. $Q$ decreases with increase in frequency and $Q \times f$ is a constant for given dielectric material. The temperature coefficient of resonant frequency ($\tau_f$) is the measure of drift of resonant frequency with temperature. For a material to be used as good DR, this drift must be minimum. A number of materials having these properties are being investigated [3,4]. Still the search for new materials having better properties is in progress. DRs based on niobates and tantalates are now gaining attention due to their good dielectric properties [5–9]. A special group of materials having the general formula $A^3B^4C^5O_{2x}$ was reported by Kazantsev et al. [10]. Maeda et al. [11] suggested the possibility of using rare earth titanium tantalates and niobates of the above group as materials suitable for microwave applications. Sebastian et al. [12] reported that SmTiNbO$_6$ ceramics of the above group can be used as a good material for DR applications and later they reported the microwave dielectric properties of other lanthanide-based niobates [13]. Surendran et al. [14] reported the microwave dielectric properties of lanthanide-based titanium tantalates. Various lanthanide systems of this group are reported for their good optical properties. Recently photoluminescence studies of certain polycrystalline lanthanide titanium tantalates are reported by Jacob et al. [15]. EuTiNbO$_6$, EuTiTaO$_6$, and Y$_{0.5}$Eu$_{0.5}$TiNbO$_6$ were reported as good scintillators for gamma ray and neutron registration [16]. Kazantsev et al. [10] reported that the LnTiTaO$_6$ compounds with lanthanides of atomic numbers in the range 57–66 have orthorhombic aeschynite structure and those in the range 67–71 have orthorhombic euxenite structure. The principle difference between Ln$^{3+}$ in these structures is that in aeschynite structure they lie in closely connected chains where as in euxenite structures in densely packed parallel planes [17]. Surendran et al. [14] reported that LnTiTaO$_6$ ceramics with aeschynite orthorhombic structures have positive $\tau_f$ with higher dielectric...
constant while those having euxenite orthorhombic structure have negative $\tau_f$ with relatively lower dielectric constant.

Generally materials with high permittivity have a positive temperature coefficient of resonant frequency ($\tau_f$) [18]. The materials with identical crystal structures and having opposite $\tau_f$ can be combined in suitable ratios to get near zero $\tau_f$ with improvement in their dielectric properties. A number of efforts are reported to reduce the $\tau_f$ by making suitable solid solutions of materials with positive and negative $\tau_f$ [19–22] and also using suitable dopants [23–25]. Solomon et al. [26], Surendran et al. [27,28] reported that by making a suitable solid solutions of both aeschynite and euxenite structures, it is possible to get compositions having low $\tau_f$ and desirable microwave dielectric properties. Oishi et al. [29] reported the microwave dielectric properties and crystal structure of Sm(Nb$_{1-x}$Ta$_x$)(Ti$_{1-y}$Zr$_y$)O$_6$ ceramics. Recently we have reported the effect of yttrium substitution for Nd on NdTiTaO$_6$ ceramics and obtained near zero temperature coefficient of resonant frequency ($\tau_f$) along with good dielectric properties [30]. In this paper we report the synthesis, characterization and microwave dielectric properties of Ce$_x$Y$_{1-x}$TiTaO$_6$ ceramics.

2. Experimental

Conventional solid-state ceramic route was used to prepare polycrystalline samples in the form of thick cylinders. High purity CeO$_2$, Y$_2$O$_3$, TiO$_2$ (CDH, 99.9%) and Ta$_2$O$_5$ (NFC, 99.9%) were weighed in stoichiometric ratios and mixed thoroughly in acetone medium in a ball mill for 2 h. The powder was dried and then calcined at 1300 $^\circ$C for 5 h in electrically heated furnace. The calcined powder was again ground well for 2 h in the ball mill with acetone as the wetting medium. The specimen was again dried well and 5% polyvinyl alcohol was added as a binder and again ground well and dried. The powder was then pressed in the form of a cylindrical pellet at a pressure of 150 MPa using hydraulic press. The pellets were then sintered in a controlled heating schedule of 4 $^\circ$C/min up to 600 $^\circ$C and soaked for 1 h to expel polyvinyl alcohol. This was followed by heating the samples at a rate of 5 $^\circ$C/min up to the optimized sintering temperature with a soaking time of 4 h. The samples were then furnace cooled to room temperature. The sintered density of well polished samples was measured using Archimedes method. Powdered samples were used for X-ray diffraction (Philips Expert Pro) studies using Cu K$\alpha$ radiation. The cell parameters were calculated using least square method and then the theoretical densities were calculated. To confirm the XRD results, Raman spectra of selected samples were recorded and analyzed with a Bruker RFS100/S spectrometer (resolution of 4 cm$^{-1}$ from 50 to 1000 cm$^{-1}$ using Nd:YAG laser source, lasing at 1064 nm and power 150 mW and by a germanium diode detector). Polished samples were thermally etched at 1500 $^\circ$C and were used for scanning electron microscopy (SEM) (JEOL JSM 5610 LV). The dielectric properties of the samples were measured in the microwave frequency region using cavity resonator method with the network analyzer (Agilent 8753 ET) and the variation of resonant frequency with temperature was measured with the help of Keithley 2000 multimeter attached with Keithley 2001 model TC scanner. The temperature coefficient of resonant frequency ($\tau_f$) was also measured over a range of temperature 30–70 $^\circ$C.

3. Results and discussion

Fig. 1a shows the XRD patterns of Ce$_x$Y$_{1-x}$TiTaO$_6$ for $x = 0, 0.2, 0.4, 0.6, 0.8$ and $1$. It can be seen that at $x = 0.2$, reflections of both aeschynite and euxenite structures are present but from $x = 0.4$ to 1 the reflections are only that of aeschynite structure. For a better understanding, XRD patterns are recorded for $x = 0.22, 0.24$ and 0.3 and are shown in Fig. 1b. The peak shown as (*) is the reflection of euxenite structure which is present from $x = 0.2$ to 0.3. Thereafter this peak disappears and this implies for $x = 0.2, 0.24$ and 0.3 are composite in nature and for $x \geq 0.4$ solid solutions are formed. No phases other than aeschynite and euxenite structure are observed in the XRD patterns. For a better understanding Raman spectra of selected samples are recorded and are shown in Fig. 2. Paschoal et al. [32] reported the Raman scattering study of RETiTaO$_6$ dielectric ceramics for the $R = Al, Y, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er$ and Yb. They clearly differentiated compounds with aeschynite and euxenite structure based on the characteristic Raman bands. Comparing the spectral data obtained in the present work with that of Paschoal et al. [32], it is found that the data exactly match with the results derived from the XRD patterns. The structure of the compositions with $x = 0$ is exactly euxenite and that of $x = 0.4$ is exclusively aeschynite. The compositions with $x = 0.2$ and 0.24 contain characteristics bands of the two structures. The characteristic Raman band at wave number $>800$ cm$^{-1}$ is obtained in the range 853–856 cm$^{-1}$ for $x = 0, 0.2$ and 0.24 and at 868 cm$^{-1}$ for $x = 0.4$. It is reported that this band is observed in the range 854–857 cm$^{-1}$ in the euxenite structure and in the range 864–869 cm$^{-1}$ in the aeschynite structure. The spectrum for $x = 0.4$ is found to be exactly similar to that of CeTiTaO$_6$ [32]. This confirms that the composition with $x = 0.4$ has the same structure of CeTiTaO$_6$, which is reported as aeschynite. As shown by the XRD pattern the Raman spectra for $x = 0.2$ and 0.24 shows that the major phase is aeschynite itself. However the bands at 853 and 413 cm$^{-1}$ for $x = 0.2$ and that at 853 cm$^{-1}$ and the weak broad band
centered at 416 cm\(^{-1}\) for \(x = 0.24\) show euxenite phase in the compounds. Thus the Raman and X-ray analysis confirms for \(x = 0.2, 0.24\) and 0.3 are composite in nature and for \(x \geq 0.4\) solid solutions are formed.

The lattice parameters and theoretical densities calculated from the XRD patterns and are given in Table 1. Since the compositions \(x = 0.2, 0.24\) and 0.3 are composite in nature, their lattice parameters are not calculated. There is a gradual increase in theoretical density with respect to the increase in the concentration of Ce.

Table 1

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a (\text{Å}))</th>
<th>(b (\text{Å}))</th>
<th>(c (\text{Å}))</th>
<th>Theoretical density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.6545</td>
<td>5.5594</td>
<td>5.1904</td>
<td>6.53</td>
</tr>
<tr>
<td>0.4</td>
<td>5.2777</td>
<td>10.9342</td>
<td>7.4243</td>
<td>6.769</td>
</tr>
<tr>
<td>0.6</td>
<td>5.3096</td>
<td>10.9389</td>
<td>7.4519</td>
<td>6.859</td>
</tr>
<tr>
<td>0.8</td>
<td>3.6599</td>
<td>10.9304</td>
<td>7.4886</td>
<td>6.915</td>
</tr>
<tr>
<td>1</td>
<td>5.3894</td>
<td>10.9350</td>
<td>7.5252</td>
<td>7.003</td>
</tr>
</tbody>
</table>

Fig. 2. Raman spectra of Ce\(_{x}\)Y\(_1\)TiTaO\(_6\) with \(x = 0, 0.2, 0.24,\) and 0.4.

Table 2

<table>
<thead>
<tr>
<th>(x)</th>
<th>Diameter ((x10^{-2}) m)</th>
<th>Length ((x10^{-2}) m)</th>
<th>Resonant frequency, (f) (GHz)</th>
<th>(Q_\circ \times f) (GHz)</th>
<th>Dielectric constant, (\varepsilon_r)</th>
<th>(\tau_f) (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.27</td>
<td>7.01</td>
<td>5.720</td>
<td>38,600</td>
<td>17.6</td>
<td>-52.2</td>
</tr>
<tr>
<td>0.2</td>
<td>12.35</td>
<td>6.95</td>
<td>4.686</td>
<td>33,700</td>
<td>26.0</td>
<td>-12.0</td>
</tr>
<tr>
<td>0.22</td>
<td>12.10</td>
<td>6.85</td>
<td>4.702</td>
<td>27,000</td>
<td>28.8</td>
<td>-3.6</td>
</tr>
<tr>
<td>0.24</td>
<td>6.80</td>
<td>4.549</td>
<td>29,500</td>
<td>28.7</td>
<td>34.5</td>
<td></td>
</tr>
<tr>
<td>0.26</td>
<td>12.25</td>
<td>6.85</td>
<td>4.498</td>
<td>22,700</td>
<td>29.4</td>
<td>1.3</td>
</tr>
<tr>
<td>0.3</td>
<td>12.72</td>
<td>7.10</td>
<td>4.284</td>
<td>32,500</td>
<td>32.5</td>
<td>4.0</td>
</tr>
<tr>
<td>0.4</td>
<td>12.10</td>
<td>6.99</td>
<td>4.093</td>
<td>25,500</td>
<td>34.6</td>
<td>34.8</td>
</tr>
<tr>
<td>0.6</td>
<td>6.98</td>
<td>3.984</td>
<td>20,200</td>
<td>36.6</td>
<td>34.0</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>12.01</td>
<td>6.98</td>
<td>3.887</td>
<td>15,400</td>
<td>39.4</td>
<td>57.5</td>
</tr>
<tr>
<td>1</td>
<td>12.28</td>
<td>6.95</td>
<td>3.816</td>
<td>11,500</td>
<td>39.5</td>
<td>60.1</td>
</tr>
</tbody>
</table>

Fig. 3a–c shows the SEM images of Ce\(_x\)Y\(_1\)TiTaO\(_6\) ceramics. It was reported that [27,31] aeschynite structured LnTiTaO\(_6\) ceramics have elongated grains, while for euxenite ceramics have typical equiaxed grains. Similar grains are observed in Fig. 3a and c. In
Fig. 3b, both types of grains are present. This implies the formation of composite of both aeschynite and euxenite structures in Ce$_{0.24}$Y$_{0.76}$TiTaO$_6$ system. This result is in good agreement with the XRD results. These images also reveal that the samples are well sintered with minimum porosity.

The microwave dielectric properties of sintered Ce$_x$Y$_{1-x}$TiTaO$_6$ ceramics are given in Table 2. The variation of dielectric constant and temperature coefficient of resonant frequency are shown in Fig. 4. The dielectric constant is found to increase with the increase in concentration of Ce. The temperature coefficient of resonant frequency ($\alpha_f$) also shows a similar variation. All the samples have high $Q_u \times f$ and hence they are good electronic materials for microwave applications.

4. Conclusion

Ce$_x$Y$_{1-x}$TiTaO$_6$ ceramics were prepared through the solid-state ceramic route. The coexistence of both euxenite and aeschynite structures for $x = 0.2, 0.24$ and 0.3 are established using X-ray diffraction, Raman spectroscopic investigations and scanning electron microscopy. Raman and X-ray analysis confirms for $x = 0.2, 0.24$ and 0.3 are composite in nature and for $x \geq 0.4$ solid solutions are formed. The dielectric constant increases with higher concentrations of Ce. Very low temperature coefficient of resonant frequency was obtained for the compositions Ce$_{0.2}$Y$_{0.78}$TiTaO$_6$, Ce$_{0.24}$Y$_{0.76}$TiTaO$_6$, Ce$_{0.26}$Y$_{0.74}$TiTaO$_6$ and Ce$_{0.3}$Y$_{0.7}$TiTaO$_6$. These compositions with relatively high $\varepsilon_t$ (>28) and high $Q_u \times f$ (>22,000) are potential candidates for practical applications.

Acknowledgements

We are grateful to Dr. M.T. Sebastian for his help and encouragement during this work. The authors Sam Solomon and H. Padma Kumar are thankful to Kerala State Council for Science, Technology and Environment (KSCSTE) for financial assistance. The help of Dr. Sivakumar of Annamalai University in SEM analysis is acknowledged.

References