Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 23 (2003) 2661–2666

www.elsevier.com/locate/jeurceramsoc

Raman scattering study of RETiTaO$_6$ dielectric ceramics

C.W.A. Paschoal[a], R.L. Moreira[a,*], C. Fantini[a], M.A. Pimenta[a],
K.P. Surendran[b], M.T. Sebastian[b]

[a]Departamento de Física—ICEx, UFMG, C.P. 702, 30161-970, Belo Horizonte, MG, Brazil
[b]Ceramics Technology Division, Regional Research Laboratory, Trivandrum, 695 019 India

Abstract

In this work we have investigated microwave-dielectric ceramics RETiTaO$_6$ (RE = Al, Y, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Yb) by Raman scattering measurements at room temperature. The observed Raman-active phonons were analysed in conformity with two orthorhombic structures proposed for these ceramics, namely aeschynite (for lanthanide ions with atomic number between 58 and 66) or euxenite (for Y, Ho, Er and Yb). The results indicate that the phonon spectra remained relatively unchanged with respect to the RE ion substitution within each structure. For the three remaining materials with RE = La, Al and In, which are known to present multiphases, the Raman phonon spectra showed significant differences in comparison with those of ceramics with aeschynite and euxenite structure.

Keywords: Dielectric ceramics; Microwave resonators; Raman spectroscopy; RETiTaO$_6$

1. Introduction

In recent years there has been increasing interest in materials for use as microwave dielectric resonators (hereafter DR), due to the rapid advances in telecommunication and satellite broadcasting. DR materials exhibit remarkable advantages when compared with other materials, as compactness, light weight, thermal stability and low production cost. A good DR material must match the following conditions: present a high real part of the dielectric constant (since that the resonator size is proportional to $1/\sqrt{\varepsilon'}$), a high quality factor Q at the operating frequency (to allow selectivity), and a low temperature coefficient of the resonant frequency τ_f (to provide stability). Moreover, high dielectric permittivity materials can be employed in integrated capacitor gate insulators for metal-oxide-semiconductor devices and RAM memories. In recent years, several materials have been investigated for practical applications. The main compounds studied have been complex perovskites or related structures such as (Zr, Sn)TiO$_4$,[1] BaO–TiO$_2$–Nb$_2$O$_5$/Ta$_2$O$_5$,[2] BaO–TiO$_2$–RE$_2$O$_5$ (RE = La, Nd, Sm and Pr),[3] Ba(A$_{1/3}$B$_{2/3}$)O$_3$ (Ref. 4) and RE(AB)O$_6$ (Refs. 5–7) (RE a rare-earth ion and A = Ti, Hf ; B = Nb, Ta).

Particularly, the RE(AB)O$_6$ system has been characterized of the view of their microwave properties and several materials have been proposed as possible DR such as SmTiNbO$_6$, EuTiNbO$_6$, ErTiTaO$_6$, EuTiTaO$_6$ and YTiTaO$_6$.[5–7] Attempts have been made to partially replace one rare earth with another in the (RE$_{1-x}$RE$_x$')TiNbO$_6$ system in an effort to develop a near to zero τ_f ceramic and improve the microwave dielectric properties with relative success.[8] Optical spectroscopy studies of RETiNbO$_6$ (RE = Nd, Pr and Er) single crystals[9–12] suggested that these compounds are possible candidates as gain media in microlasers. Thus, a vibrational study of this system is very important, as well regarding laser applications, where it is necessary to have a low cut-off frequency in the phonon spectra in order to reduce non-radiative decays, as well as for microwave applications, where the optical phonon characteristics determine completely the dielectric response in the microwave region. Since vibrational investigations of the system RETiTaO$_6$ and RETiNbO$_6$ are still lacking, we have performed a systematic investigation on the vibrational optical phonons of these promising DR ceramics. In this work, we report the Raman scattering measurements in RETiTaO$_6$ dielectric ceramics for RE = Al, Y, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Yb.

---

* Corresponding author. Tel.: +55-31-3499-5629; fax: +55-31-3499-5600.
E-mail address: bmoreira@fisica.ufmg.br (R.L. Moreira).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00141-9

2. Experiment

The RETiTaO$_6$ 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 in stoichiometric proportions and were ball milled using polyethylene mill bottle using zirconia balls in distilled water for 48 h. The slurry was dried at 100 °C in an oven and calcined at 1250 °C for 8 h with intermediate grinding. Exceptions were AlTiTaO$_6$ and InTiTaO$_6$ that were calcined at a lower temperature of 1200 °C. Each material was then ground for several hours in an agate mortar. A 5 wt.% of poly vinyl alcohol was added as binder and the powders 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 heated at a rate of 5 °C/min up to 600 °C and held at 600 °C for 1 h, to expel the binder, before they were sintered in the temperature range 1500–1625 °C, for 4 h in air (heating rate of 10 °C/h). The sintering temperature varied with composition. The optimum sintering temperature corresponded to the condition yielding best dielectric properties in the microwave region. Most of the RETiTaO$_6$ ceramics were sintered to above 95% of their theoretical densities. These ceramic pellets were smooth enough for use in Raman spectroscopy without any additional polishing.

Micro-Raman scattering measurements were carried out at room temperature using a triple-monochromator DILOR XY spectrometer equipped with an Olympus microscope. The samples were excited with either the 514.5 nm or the 488 nm line of an Argon–Krypton ion laser and the backscattered light was collected in a LN$_2$-cooled CCD detector. All slits and optics of the spectrometers were set to give a spectral resolution better that 2 cm^{-1}. All measurements were performed using a long-working-distance plano-achromatic objective (50×/80×/100×).

3. Group theory analysis

According to Surendran et al., [7] RETiTaO$_6$ 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. Thus, these crystals contain 36 atoms in the primitive cell, corresponding to 108 degrees of freedom that can be reduced in terms of representations of the D_{2h} factor group at the Γ-point of the first Brillouin zone. In this structure, the RE ions occupy a $C_s^{xy}(4)$ site; the Ti/Ta ions occupy $C_1(8)$ sites of general symmetry; there are two distinct oxygen ions in $C_1(8)$ sites of general symmetry and two distinct oxygen ions in $C_s^{xy}(4)$ sites. Using the method of factor–group analysis proposed by Rousseau et al.[13] we can calculate the corresponding mode distribution due to this site occupation as: $B_{1u}+B_{2u}+B_{3u}$ (acoustic), $15A_g+12B_{1g}+15B_{2g}+12B_{3g}$ (Raman), $14B_{1u}+11B_{2u}+14B_{3u}$ (infrared) and $12A_u$ (silent). Thus, up to 54 optical modes are expected in the Raman spectra.

For Y and RE ions with atomic number higher than 67, the crystal exhibits an euxenite orthorhombic Pbcn $\left(D_{2h}^{14}\right)$ structure, with four molecules per unit cell, and, therefore, there are 108 degrees of freedom. However, in this structure, while the RE ions still occupy a $C_s^{xy}(4)$ site and the Ti/Ta ions occupy $C_1(8)$ sites of general symmetry, the three distinct oxygen ions occupy now $C_1(8)$ sites of general symmetry. By using the factor–group analysis, we obtain the corresponding mode distribution in terms of irreducible representations of the D_{2h} factor group at the Γ-point corresponding to these site occupation: $B_{1u}+B_{2u}+B_{3u}$ (acoustic), $14A_g+13B_{1g}+14B_{2g}+13B_{3g}$ (Raman), $13B_{1u}+12B_{2u}+13B_{3u}$ (infrared) and $13A_u$ (silent). Thus, in spite of the differences in the irreducible representation decompositions, the number of the predicted Raman modes remain unchanged.

For the case of LaTiTaO$_6$, the ceramic shows multi phases[7] such as La$_2$Ti$_2$O$_7$ and TaO$_5$. An analogous situation is observed for InTiTaO$_6$, when phases such as In$_2$TiO$_5$ and InTaO$_4$ are present.[7] The compound AlTiTaO$_6$ presents tetragonal cassiterite structure and is considered as a solid solution, since Ta$_2$O$_5$ and TiO$_2$ have the same structure and the Al ions can be substituted for Ti and Ta ions.[7]

4. Results and discussions

The Raman spectra were taken with two laser lines (514.5 and 488 nm) in order to separate the Raman modes from luminescence, very common in the optical spectra of RE compounds. Using this procedure, it was possible to identify that all vibrational modes (phonons) have frequencies below 900 cm^{-1}, while all higher frequency bands have an electronic origin. An interesting fact is that for all samples, except ErTiTaO$_6$, the excitation with the 514.5 nm provides only phonon bands below that 900 cm^{-1}. For ErTiTaO$_6$, nevertheless, the spectra obtained also show optical transitions in this spectral region. Fortunately, the spectrum with 488 nm only shows vibrational Raman bands. Thus, the use of only two lasers lines granted the observation of the Raman phonon modes.

The Raman spectra of the ceramics with aeschynite structure are shown in Fig. 1. As expected, there are not significant changes in the spectra for different RE ions within the same structure. This fact is quite comprehensive since the ionic radius and atomic mass do not vary significantly from one ion to another. This is better observed through the evolution of the mode

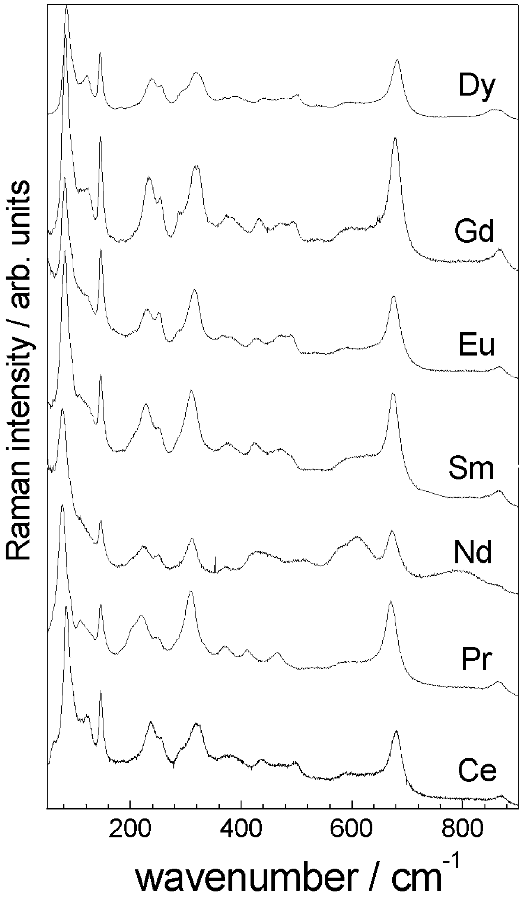

Fig. 1. Raman spectra for RETiTaO$_6$ (RE = Ce, Pr, Nd, Sm, Eu, Gd and Dy) ceramics with aeschynite structure. All spectra were excited with a 514.5 nm line. The spectra are displaced vertically for clarity.

Table 1
Raman active modes (wavenumber/damping, in cm^{-1}) observed for RETiTaO$_6$ (RE = Ce, Pr, Nd, Sm, Eu, Gd and Dy) ceramic pellets with aeschnite structure

Ce	Pr	Nd	Sm	Eu	Gd	Dy
83/13	77/16	77/16	81/15	81/12	82/12	84/11
95/16	91/9	92/18	94/8	93/9	94/13	94/17
111/19	110/14	110/13	109/21	105/20	111/21	110/15
123/16	123/18	123/10	126/17	121/9	125/14	122/16
146/8	146/10	146/9	146/9	147/8	146/8	145/9
183/6	183/7	–	–	–	–	182/5
207/15	202/16	204/26	204/18	203/19	208/15	206/8
236/26	221/25	225/25	228/27	230/24	233/24	238/25
256/13	251/15	250/16	252/14	252/12	255/13	257/13
292/16	287/27	291/26	285/12	291/19	289/17	292/18
319/31	308/21	311/21	310/29	315/24	318/29	319/33
348/41	337/15	341/25	340/24	343/17	348/13	–
372/29	372/21	372/17	370/28	365/19	370/29	367/27
394/34	–	–	387/35	384/23	389/38	393/40
436/23	411/19	424/40	426/27	428/23	432/20	440/27
472/43	464/28	456/46	467/39	471/34	471/39	475/43
498/17	484/17	499/22	489/17	492/14	495/15	501/17
541/27	523/53	511/52	532/24	534/18	534/25	540/29
593/44	592/66	576/39	596/56	591/52	596/50	595/37
635/48	640/45	613/53	640/55	645/60	647/52	643/53
680/26	671/27	673/27	675/26	676/26	679/24	681/25
–	–	–	–	–	–	809/39
816/51	821/46	–	839/39	829/59	840/60	849/35
867/30	864/25	864/34	866/28	867/31	867/25	869/39

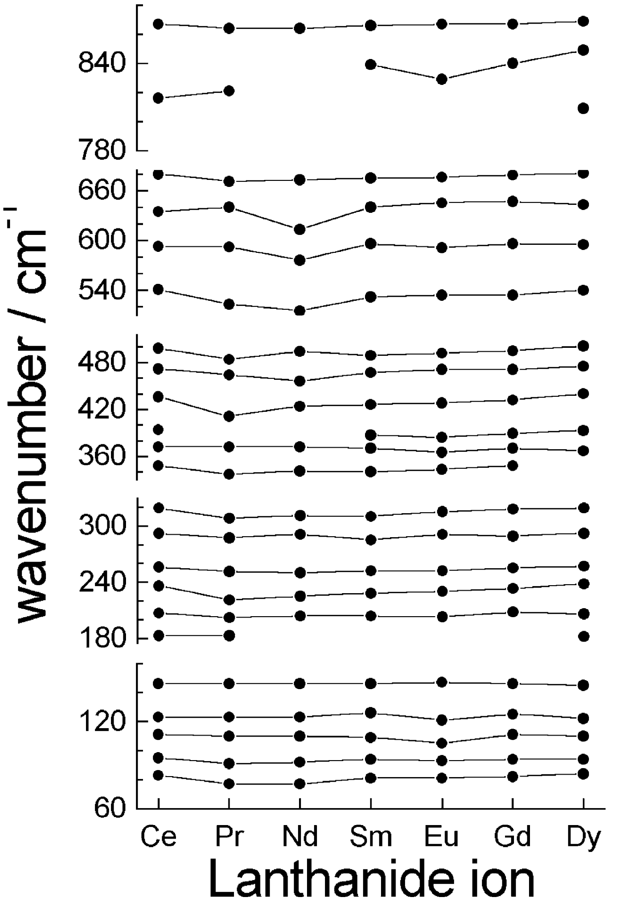

Fig. 2. Raman mode evolution with RE ion of the RETiTaO$_6$ ceramics with aeschynite structure. The ions are presented with increasing order of atomic number.

wavenumbers for different RE ions, which is presented in Fig. 2. We can observe that the wavenumber behaviour is stable with change of RE ions. The phonon characteristic (position/width) of the observed Raman modes for aeschynite structure is given in Table 1. In Figs. 1 and 2 and Table 1, the data of TbTiTaO$_6$ have been omitted, because the spectra were very poor, weak and noisy, even for long time exposures.

In Fig. 3, the Raman spectra of the ceramics with euxenite structure are presented. As in the case of the aeschynite compounds, the wavenumber mode evolution of the euxenite structure is stable with RE ion substitution, as we can see in Fig. 4. The observed Raman bands of the euxenite compounds are listed in Table 2.

In the two known structures, the Ti and Ta ions are in the centre of O$_6$ distorted octahedra. These octahedra are either joined in pairs by edge sharing, with each pair being connected to six other pairs by corner sharing in the case of the aeschynite structure, or joined by edge or corner sharing to form a double layer perpendicular to the *c*-axis in the case of the euxenite structure. However, there is no preference for octahedra centre occupation by Ti or Ta. Thus, there is occupational disorder of Ti

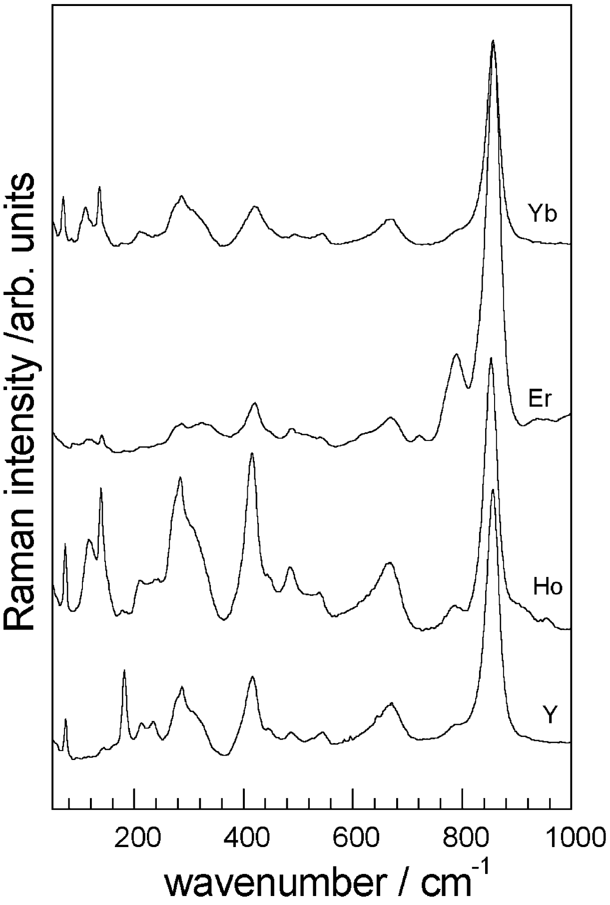

Fig. 3. Raman spectra for $RETiTaO_6$ (RE = Y, Ho, Er and Yb) ceramics with euxenite structure. All spectra were excited with a 514.5 nm line, excepted $ErTiTaO_6$ which was excited with a 488 nm line.

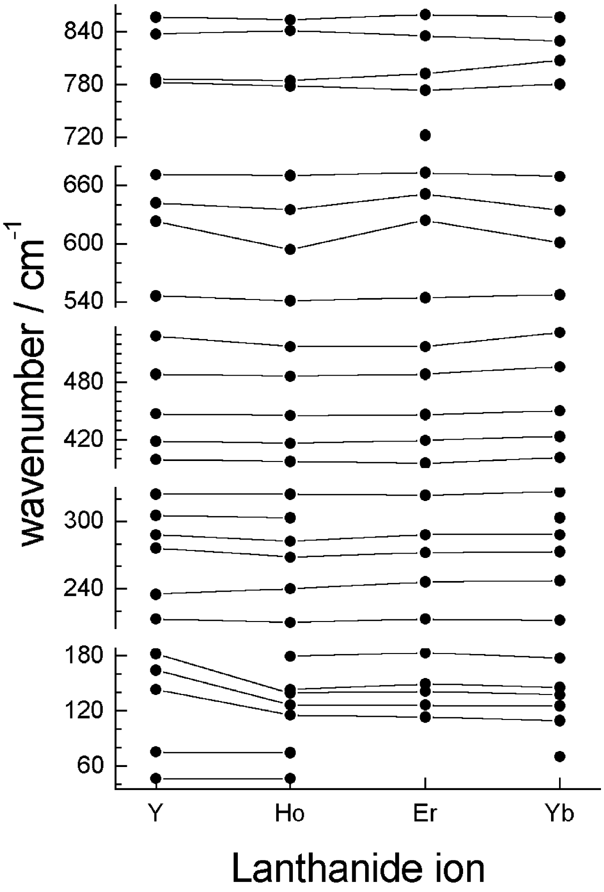

Fig. 4. Raman mode evolution with RE (increasing atomic number) of the $RETiTaO_6$ ceramics with euxenite structure.

or Ta ions at these positions. This fact is evidenced by the presence of large damping parameters of some modes for aeschynite and euxenite compounds (see Tables 1 and 2). Moreover, the octahedra in both structures are distorted and this leads to different bond lengths, which is responsible for the broadening of the modes associated with Ti or Ta–O vibrations (stretching and bending).

The number of modes depicted for compounds with aeschynite and euxenite structure was around 22–26 for each compound, while 54 were predicted by factor group analysis for both structures. The smaller number of observed modes than predicted by theory can be explained by the broadening of the bands due the Ti/Ta occupational disorder and the octahedra distortion discussed earlier. Therefore, the broad bands obscure the weak modes.

Unfortunately, since the octahedra are joined and coupled, a molecular site group analyses cannot be performed for the TiO_6 and TaO_6 octahedra, in order to separate their internal modes. However, by considering the positions of the modes associated with these octahedra in other similar oxide polyhedral materials,[14] it is possible to separate the spectra of our materials in some regions with specific modes. Thus, the bands with wavenumbers greater than 450 cm^{-1} can be associated with several modes involving the stretching of the Ta–O bonds. For wavenumber between 200 and 450 cm^{-1}, the bands are due, principally, to the bending of O–Ta–O and O–Ti–O and the stretching Ti–O vibrations. The origin of the bands with wavenumbers below 200 cm^{-1} would be lattice vibrations, mainly associated to RE ions. This fact is better evidenced for euxenite compounds, where the lattice modes associated to the Y ion have larger wavenumbers than those associated with the lanthanide ions (Ho, Er and Yb) due to the considerable mass difference, as we can observe in the Fig. 4 and in the Table 2. A relationship between the modes associated with these ions can be obtained by taking a simple mass-spring model for the vibrations. Then, $\tilde{\nu}_Y/\tilde{\nu}_{RE} \approx \sqrt{m_{RE}/m_Y}$, where $\tilde{\nu}_Y(\tilde{\nu}_{RE})$ is the wavenumber associated with Y(RE) ion and $m_Y(m_{RE})$ is the corresponding mass of the Y(RE) ion. The Y modes that satisfy this relationship are located at around 143, 164 and 182 cm^{-1}. The isolated modes below 90 cm^{-1} can be associated with the octahedral displacements due to

Table 2
Raman active modes (wavenumber/damping, in cm^{-1}) observed for RETiTaO$_6$ (RE = Y, Ho, Yb and Er) ceramic pellets with euxenite structure

Y	Ho	Er	Yb
46/13	46/12	–	–
75/5	74/5	–	70/6
143/12	115/18	113/17	109/23
164/27	126/16	126/20	125/26
182/8	139/6	141/7	137/6?
–	145/21	149/11	226/30
–	177/6	183/15	–
213/19	210/15	213/21	212/21
235/22	240/53	246/35	247/49
276/25	268/13	272/20	273/20
288/16	282/21	288/24	288/16
305/34	303/27	–	303/30
324/29	324/34	323/51	326/35
–	–	368/58	–
399/28	397/26	395/22	401/31
418/23	416/22	419/22	423/28
447/29	445/35	446/36	450/34
488/30	486/28	488/28	496/36
528/29	517/29	517/29	532/25
546/17	541/22	544/23	547/16
623/60	594/69	624/58	601/25
642/26	635/46	651/35	634/37
671/38	670/40	673/30	669/40
–	–	722/13	–
782/32	778/17	773/30	780/17
802/42	789/14	792/28	796/23
837/33	841/22	835/35	829/30
856/28	854/26	856/46	857/27

their higher masses. We can observe that they do not vary for the different RE ions.

It is noteworthy to point out the differences between spectra of the aeschynite and euxenite structures. Fig. 5 shows the Raman spectra for RE = Dy (aeschynite) and Ho (euxenite), chosen because they are in the border line between the two structures. We can see that for low (<200 cm^{-1}) and high (> 550 cm^{-1}) wavenumbers the spectra are practically the same, presenting no significant changes at the position and damping of the modes. However, at the mid-wavenumber region, significant differences are observed in the spectra. Since most of RETiTaO$_6$ ceramics crystallize in either, aeschynite or euxenite structure, this spectral region can be used to distinguish the different structures.

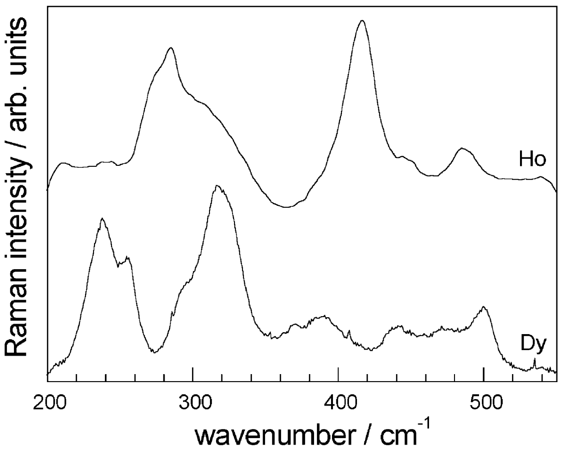

Fig. 5. Comparison between Raman spectra of HoTiTaO$_6$ and DyTiTaO$_6$ ceramics.

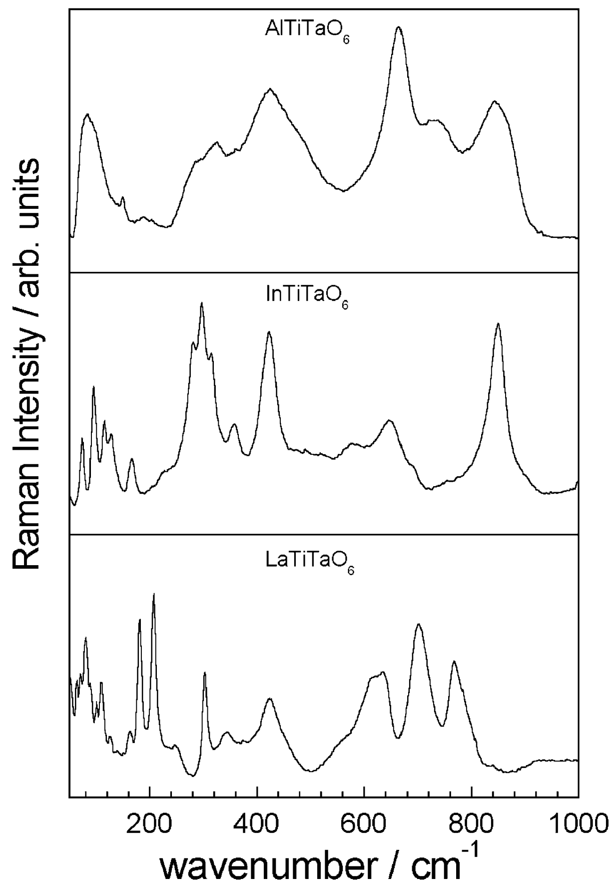

Fig. 6. Raman spectra for RETiTaO$_6$ (RE = La, In and Al) ceramics.

The spectra of RE = Al, In and La ceramics, presented in Fig. 6, are very distinct from those presented by materials with aeschynite and euxenite structures. This is likely to be due to the multiphases exhibited by these compounds, as evidenced by other techniques.[7] Efforts to analyse the vibrational and structural behaviours of these materials are in progress and will be published elsewhere.

5. Conclusions

In this work, we have performed a Raman scattering study of the microwave dielectric system RETiTaO$_6$ for 15 different lanthanides or isovalence ions. The spectra of the lanthanides could be arranged in two groups, those of aeschynite compounds (lanthanides with atomic numbers lowers and equal than 66) and those for euxenite structures (Yttrium and lanthanides with atomic number higher than 66). The spectra for the other non-lanthanide ions were very complex due to the presence of multiphases. The Raman-active phonons showed high stability with the substitution of the RE ion of both structures, aeschynite and euxenite. Around 22–26 broad bands were observed for each compound. This fact was associated with the occupational disorder of Ti/Ta ions at O_6 octahedra centre, besides octahedral distortion. The main differences between the aeschnite and euxenite Raman spectra are located in the mid-wavenumber region of the spectrum, between 200 and 550 cm^{-1}, showing that the way the octahedral are joined reflects in their vibrational modes.

Acknowledgements

The Brazilian authors are grateful to the Brazilian founding agencies CNPq and FAPEMIG and to the Millennium Science Initiative: "Water—a mineral approach" for financial support towards this work. The Indian authors are grateful to the Department of Science and Technology, New Delhi for financial support.

References

1. Christoffersen, R., Davies, P. K., Wei, X. H. and Negas, T., Effect of Sn substitution on cation ordering in $(Zn_{1-x}Sn_x)TiO_4$ microwave dielectric ceramics. *J. Am. Ceram. Soc.*, 1994, **77**, 1441–1450.
2. Sebastian, M. T., New low loss microwave dielectric ceramics in the $BaO–TiO_2–Nb_2O_5/Ta_2O_5$ system. *J. Mater. Sci.: Mater. Electron.*, 1999, **10**, 475–478.
3. Laffez, P., Desgardin, G. and Raveau, B., Influence of calcinations, sintering and composition upon microwave properties of $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$-type oxide. *J. Mater. Sci.*, 1992, **27**, 5229–5238.
4. Chen, X. M., Suzuki, Y. and Sato, N. J., Sinterability improvement of $Ba(Mg_{1/3}Ta_{2/3})O_3$ dielectric ceramics. *J. Mater. Sci.: Mater. Electron.*, 1994, **5**, 244–247.
5. Sebastian, M. T., Ratheesh, R., Sreemoolanadhan, H., Solomon, S. and Mohanan, P., Samarium titanium niobate ($SmTiNbO_6$): a new microwave dielectric ceramic. *Mat. Res. Bull.*, 1997, **32**, 1279–1284.
6. Sebastian, M. T., Solomon, S. and Ratheesh, R., Preparation, characterization and microwave properties of $RETiNbO_6$ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, and Yb) dielectric ceramics. *J. Am. Ceram. Soc.*, 2001, **84**, 1487–1489.
7. Surendran, K. P., Solomon, S., Varma, M. R., Mohanan, P. and Sebastian, M. T., Microwave dielectric properties of $RETiTaO_6$ (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er, Yb, Al and In) ceramics. *J. Mat. Res.*, 2002, **17**, 2561–2566.
8. Solomon, S., Kumar, M., Surendran, K. P., Sebastian, M. T. and Mohanan, P., Systhesis, characterization and properties of $[RE_{1-x}RE'_x]TiNbO_6$ dielectric ceramics. *Mat. Chem. Phys.*, 2001, **67**, 291–293.
9. Qi, X., Illingworth, R., Gallenger, H. G., Han, T. P. J. and Henderson, B., Potential laser gain media with stoichiometric formula $RETiNbO_6$. *J. Crystal Growth*, 1996, **160**, 111–118.
10. Qi, X., Han, T. P. J., Gallenger, H. G., Henderson, B., Illingworth, R. and Ruddock, I. S., Optical spectroscopy of $PrTiNbO_6$, $NdTiNbO_6$ and $ErTiNbO_6$. *J. Phys. Condens. Matter*, 1996, **8**, 4837–4845.
11. Qi, X., Han, T. P. J., Gallenger, H. G. and Henderson, B., Energy upconversion process in Er^{3+} and Nd^{3+} doped $RETiNbO_6$ crystals. *Opt. Commmun.*, 1997, **140**, 65–69.
12. Qi, X., Gallenger, H. G., Han, T. P. J. and Henderson, B., Modified Czochralski growth and characterization of $RETiTaO_6$ crystals. *J. Crystal Growth*, 1997, **180**, 73–80.
13. Rousseau, D. L., Bauman, R. P. and Porto, S. P. S., Normal mode determination in crystals. *J. Raman Spectroscopy*, 1981, **10**, 253–290.
14. Dobal, P. S., Katiyar, R. S., Jiang, Y., Guo, R. and Bhalla, A. S., Structural modifications in titania-doped tantalum pentoxide crystals: a Raman scattering study. *Int. J. Inorg. Mat.*, 2001, **3**, 135–142.