J. Braz. Chem. Soc., Vol. 15, No. 6, 890-896, 2004.
Printed in Brazil - ©2004 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Photoluminescence Behavior of the Sm^{3+} and Tb^{3+} Ions Doped Into the $Gd_2(WO_4)_3$ Matrix Prepared by the Pechini and Ceramic Methods

Cláudia A. Kodaira[a]***, Hermi F. Brito***[*,a]***, Ercules E. S. Teotonio***[a]***, Maria Cláudia F. C. Felinto***[b]***,***
Oscar L. Malta[c] ***and Giancarlo E. S. Brito***[d]

[a]*Instituto de Química, Universidade de São Paulo, CP 26077, 05508-900 São Paulo - SP, Brazil*

[b]*Instituto de Pesquisas Energéticas e Nucleares, Av. Lineu Prestes 2242, Cidade Universitária,*
05508-970 São Paulo -SP, Brazil

[c] *Departamento de Química, CCEN, Universidade Federal de Pernambuco, Cidade Universitária,*
50670-901 Recife - PE, Brazil

[d]*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo - SP, Brazil*

Os compostos $Gd_2(WO_4)_3$:RE^{3+} (onde RE = Sm e Tb) preparados via métodos Pechini e cerâmico foram caracterizados por difratometria de raios-X e espectroscopia de absorção na região do infravermelho. Estes materiais de terras raras apresentam alta intensidade luminescente, laranja para os compostos de Sm^{3+} e verde para os de Tb^{3+}, quando excitados com radiação UV. Os espectros de excitação dos compostos mostraram bandas largas oriundas da transferência de carga ligante-metal ($O\rightarrow W$ e $O\rightarrow RE^{3+}$) e bandas estreitas associadas às transições intraconfiguracionais (4f-4f). Os espectros de excitação do sistema com Tb^{3+} também exibiram bandas largas atribuídas à transição interconfiguracional (4f-5d). Quando os espectros de emissão dos compostos contendo Sm^{3+} e Tb^{3+} são obtidos com excitação no íon observa-se somente transições finas ${}^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2 e 11/2) e ${}^5D_4\rightarrow{}^7F_J$ (J = 0-6). Por outro lado, quando a excitação é monitorada na banda de transferência de carga (BTC, 270 nm) são também observadas bandas largas atribuídas a BTC ($O\rightarrow W$). Os parâmetros de intensidade experimentais, η_{Sm} e η_{Eu}, apresentaram comportamentos similares, sugerindo que o íon Sm^{3+} encontra-se em um ambiente químico altamente polarizável e que o caráter covalente da interação metal–ligante é semelhante àquele do sistema tungstato de európio. O processo de relaxação cruzada baseado nos níveis ${}^5D_3$ e ${}^5D_4$ do sistema $Gd_2(WO_4)_3$:Tb^3 foi reportado.

The $Gd_2(WO_4)_3$:RE^{3+} compounds (where RE^{3+} = Sm and Tb) were prepared by the Pechini and ceramic methods and characterized by X-ray diffraction and infrared spectroscopy. These rare earth materials present high orange (Sm^{3+}-compound) and green (Tb^{3+}-compound) luminescence intensity under UV radiation. The excitation spectra of these compounds presented broad bands arising from ligand-to-metal charge transfer ($O\rightarrow W$ and $O\rightarrow RE^{3+}$) and narrow bands from 4f-intraconfigurational transitions. The excitation spectra of Tb^{3+} system also exhibit broad bands attributed to the interconfigurational transition (4f-5d). The emission spectra exhibited the ${}^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) and ${}^5D_4\rightarrow{}^7F_J$ (J = 0-6) transitions (direct excitation), for the systems doped with Sm^{3+} and Tb^{3+}, respectively, while a broad band assigned to the LMCT ($O\rightarrow W$) is observed when the excitation is monitored on the $O\rightarrow W$ LMCT state around 270 nm. The experimental intensity parameters η_{Sm} and η_{Eu} present similar behaviors, suggesting that the Sm^{3+} ion is in a highly polarizable chemical environment with similar covalent character of the metal-donor atom interaction to the tungstate doped europium system. The cross-relaxation process from the ${}^5D_3$ to the ${}^5D_4$ levels of the $Gd_2(WO_4)_3$:Tb^{3+} system has been also reported.

Keywords: samarium, terbium, Pechini and ceramic methods, tungstate, photoluminescence

---

* e-mail: hefbrito@iq.usp.br

Introduction

The optical properties of trivalent rare earth ions (RE^{3+}) in tungstate materials, with scheelite ($CaWO_4$) structure, have been widely investigated.[1-7] The motivation for these studies has been based on their technological applications as phosphor materials in fluorescent lamps, cathode ray tubes and X-ray intensifying screens.

Since the first europium tungstate was prepared from Eu_2O_3 and tungstic acid precursors at 1000 ºC its luminescent properties[7,8] and crystal structure of $Eu_2O_3.3WO_3$ [9] have been studied. This europium system has been synthesized in different ways that generally involve high temperatures and/or a long time of heating samples. In the last decade, several low temperature preparation techniques were used to prepare fine particle systems such as co-precipitation,[10] sol-gel method[11] and hydrothermal synthesis.[12] Recently we have reported the preparation, characterization and photoluminescent studies of the $RE_2(WO_4)_3$ system (where RE = La, Eu and Gd), which was produced by the Pechini method.[13-15]

The electronic spectra of the RE^{3+} ions present narrow and low intensity bands due to the shielding of the 4f electrons from ligand field effects by the electrons of the filled 5s and 5p sub-shells.[16] The Sm^{3+} ion has an odd electron configuration ([Xe] $4f^5$) labeled as a Kramer's ion, which requires that the electronic states of this ion be at least doubly degenerate by the ligand-field for any chemical environment.[17] For all $4f^N$ configurations with odd N, the maximum number of the crystal field components for Kramer's ions with $^{2S+1}L_J$ state is J+1/2 for any symmetry lower than cubic.[18] Generally, the Sm^{3+} ion has only detectable absorption transitions below 500 nm, considering that the $^6H_{5/2}\rightarrow{}^6P_{3/2}$ transition (~ 400 nm) has the highest intensity, and consequently this rare earth ion displays a (pale) yellow color.[19] In the case of the Tb^{3+} ion, the absorption spectra exhibit only weak bands from the $^7F_6\rightarrow{}^5D_4$ transition (~487 nm) in the visible range, which has no influence on the color of Tb^{3+} compounds. On the other hand, the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (~ 640 nm) and $^5D_4\rightarrow{}^7F_6$ (545 nm) hypersensitive transitions are mainly responsible for the orange and green monochromatic emission colors of the Sm^{3+} and Tb^{3+} ions, respectively.

In the present investigation, we report the preparation of the $Gd_2(WO_4)_3$:RE^{3+} (RE = Sm and Tb) compounds using the Pechini method, based on polyesterification between citric acid and ethylene glycol, according to the procedures used for the $Eu_2(WO_4)_3$,[13] $La_2(WO_4)_3$:Eu^{3+} and $Gd_2(WO_4)_3$:Eu^{3+} systems.[14] This preparation method is known due to the low cost and versatility, producing the desired compound at reduced temperatures in contrast to the conventional ceramic method. For the purpose of comparison, a conventional ceramic method was used for preparing the $Gd_2(WO_4)$:RE^{3+} (RE = Sm and Tb) compounds. The photoluminescence properties of the systems prepared by the ceramic method were also investigated.

Experimental

The $Gd_2(WO_4)_3$ matrix doped with Sm^{3+} and Tb^{3+} ions were prepared by the Pechini method as described in references 13 and 14 using the following materials: ammonium tungstate (99.999%, Acros), RE_2O_3 (RE = Gd, Sm and Tb) (99.99%, Aldrich), ethylene glycol and citric acid (99.5%, Merck). The Sm^{3+} and Tb^{3+} ions were doped into $Gd_2(WO_4)_3$ matrix in a concentration of 5 mol%. The obtained resin was heated at 450 ºC for 2 h, resulting in a black product, which was grounded into a powder and heated at 750 ºC for 4 h. For the sake of comparison, the $Gd_2(WO_4)_3$:RE^{3+} systems (RE = Sm and Tb) were also prepared by the ceramic method,[20,21] which consists in grinding and sintering the sample twice containing a stoichiometric mixture of WO_3 (prepared from the heating of ammonium tungstate, at 450 ºC for 2 h), Gd_2O_3 and the corresponding rare earth oxide (Sm_2O_3 or Tb_2O_3) in alumina crucibles at 900 ºC for 24 h.

Infrared data were recorded on a Bomem MB 100 spectrometer by averaging 96 scans with a resolution of 4 cm^{-1}. Samples were physically mixed with KBr and pressed into self-supporting pellets. These measurements were made at room temperature in the spectral range from 4000 to 350 cm^{-1}.

The X-ray diffraction patterns of the samples were recorded using a powder goniometer (Philips diffractometer model X'PERT-MPD), Ni filtered CuKα radiation (40 kV and 40 mA), between $2 < 2\theta < 70°$, in step-scanning mode (0.6°/min).

The excitation and emission spectra of the $Gd_2(WO_4)_3$:RE^{3+} system were recorded at room and liquid nitrogen temperatures collected at an angle of 22.5º (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680) using a 450 W Xenon lamp as the excitation source. The luminescence decay curves were recorded at 298 K using the phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorimeter.

Results and Discussion

The IR spectra of the tungstates (figure not shown) present the bands according to the spectral data of the

$La_2(WO_4)_3$ and $Ce_2(WO_4)_3$ compounds, suggesting a T_d symmetry with two non-equivalent $[WO_4]$ units.[22] There is a great similarity between the spectra of the compounds, considering the 950-650 cm^{-1} region corresponding to the symmetric stretching of the O-W bond, the 830-530 cm^{-1} interval that presents anti-symmetric stretching and the 470-370 cm^{-1} region that displays bands due to the bending modes of the O-W bonds.

The X-rays diffraction patterns of the $Gd_2(WO_4)_3$ matrix doped with Sm^{3+} and Tb^{3+} ions (figure not shown) obtained by the Pechini and ceramic methods present characteristic lines of standard compound with a monoclinic (pseudo-orthorhombic) lattice.[9] according to the JCPDS card #23-1076. No peaks assigned to the Gd_2O_3 and WO_3 compounds could be observed, indicating that the $Gd_2(WO_4)_3$ compound was obtained with high purity. The diffraction lines were characteristics of a policrystalline compound. The average crystallite sizes (developed along [002], [040], [-221] and [023] directions) were estimated using the Scherrer formula.[23] The errors bars were determined as a function of the adjusted full width at half maximum (FWHM) in a fitting procedure for each analyzed peak. The values of crystallite sizes of the $Gd_2(WO_4)_3:RE^{3+}$ system prepared by the Pechini method (~ 30 nm) are smaller than those prepared by the ceramic one (~ 60 nm) (Table 1).

Table 1. Average crystallite sizes for the $Gd_2(WO_3)_3$:RE system (RE = Sm^{3+} and Tb^{3+}) developed second [h k l] directions determined by the Scherrer formula [23]

h k l	G (nm)*			
	$Gd_2(WO_3)_3$:Sm		$Gd_2(WO_3)_3$:Tb	
	Ceramic	Pechini	Ceramic	Pechini
002	61 ± 3	34 ± 1	55 ± 2	23 ± 1
040	-	29 ± 1	57 ± 2	-
-221	54 ± 2	37 ± 1	57 ± 2	25 ± 1
023	60 ± 2	28 ± 1	49 ± 3	21 ± 1

Photoluminescence investigation

The excitation spectra of the $Gd_2(WO_4)_3:Sm^{3+}$ compound prepared by the Pechini and ceramic methods are shown in Figures 1a and 1b, respectively. These photoluminescence measurements were recorded at 77 K in the spectral range from 250 to 590 nm, with emission monitored on the hypersensitive $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition (around 643 nm). In the case of the Sm^{3+} compound prepared by the Pechini method, the excitation spectrum displays a high intensity broad band around 275 nm and an overlapped low intensity band around 310 nm attributed to O→W[13] and O→Sm LMCT transitions, respectively. Besides, this excitation spectrum also contains narrow bands assigned to the $4f^5$ intraconfigurational transitions characteristic of the Sm^{3+} ion (Table 2).

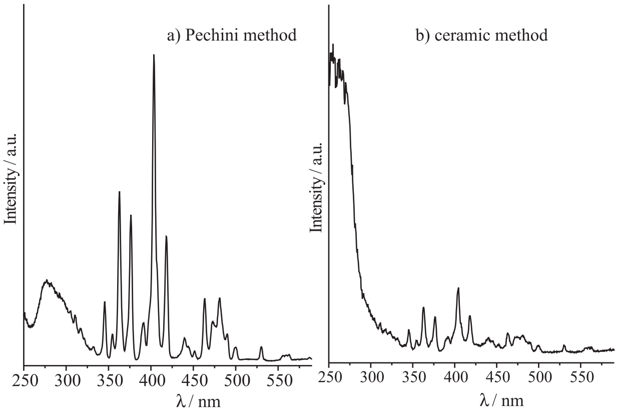

Figure 1. Excitation spectra of the $Gd_2(WO_4)_3:Sm^{3+}$ compound with emission monitored at 643 nm at liquid nitrogen temperature prepared by methods a) Pechini (750 °C) and b) ceramic (900 °C).

The excitation spectrum of the $Gd_2(WO_4)_3:Sm^{3+}$ system prepared by the ceramic method (Figure 1b) shows a broad band in the range 255-340 nm corresponding to the O→W and O→Sm LMCT with maxima at around 275 and 310 nm, respectively. The LMCT band for the system prepared by the ceramic method (Figure 1b) has higher intensity than the one prepared by the Pechini method and it is also observed the presence of narrow bands arising from the Sm^{3+} ion corresponding to the $^6H_{5/2}\rightarrow{}^{2S+1}L_J$ transitions.

The emission spectra of the Sm^{3+}-doped compounds (Figure 2), at 77 K, in the range of 500-750 nm, recorded under excitation at 404 nm, obtained by the Pechini (Figure 2a) and ceramic (Figure 2b) methods, present similar profiles. These spectra show only the bands due to 4f-4f transitions arising from the $^4G_{5/2}$ emitting level. The relatively high intensity bands are those arising from the $^4G_{5/2}\rightarrow{}^6H_J$ transitions (where J = 5/2, 7/2, 9/2 and 11/2), which are split in the maximum number of (J+1/2) components, indicating that the Sm^{3+} ion occupies a site with low symmetry. It is also observed that the forced electric dipole $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition presents the highest relative emission intensity at 643 nm.

As it can be seen, the emission spectra of the $Gd_2(WO_4)_3:Sm^{3+}$ compound recorded at 77 K (Figures 2c and 2d) monitoring the excitation on the O→W LMCT band (265 nm), show a broad band between 400 and 550 nm, with maximum at 500 nm, due to the tungstate emission. The presence of this band indicates that the energy transfer from the tungstate group to the Sm^{3+} ion is not efficient when the excitation is monitored on the LMCT band. The narrow bands assigned to the intraconfigurational-$4f^5$ transitions are also observed in those spectra (Figures 2c and 2d).

Table 2. Energy levels (in cm^{-1}) for the intraconfigurational transitions of the Sm^{3+} and Tb^{3+} ions in the $Gd_2(WO_4)_3$ matrix prepared by the ceramic method

$Gd_2(WO_4)_3$:Sm^{3+}		$Gd_2(WO_4)_3$:Tb^{3+}			
Transition	Energy (cm^{-1})	Transition	Energy (cm^{-1})	Transition	Energy (cm^{-1})
Excitation		Excitation		$^5D_4\rightarrow^7F_5$	18429
$^6H_{5/2}\rightarrow$		$^7F_6\rightarrow$			18389
$^4D_{7/2}$,$^4D_{9/2}$	28943		23923		18362
$^4D_{3/2}$,$^4P_{5/2}$	28169	$^5H_7$	29411		18281
	27548	$^5L_6$	28490		18261
$^4D_{1/2}$,$^4L_{17/2}$, $^6P_{7/2}$	26560	$^5L_9$, $^5G_4$	27894		18228
$^4H_{11/2}$,$^6M_{15/2}$, $^4M_{21/2}$	25477	$^5G_5$	27027		18188
$^6P_{3/2}$,$^4F_{7/2}$, $^4L_{13/2}$	24721	$^5L_{10}$	6490		
$^4M_{19/2}$,$^6P_{5/2}$	23923	$^5G_6$	20491	$^5D_4\rightarrow^7F_4$	17217
$^4I_{15/2}$,$^4G_{9/2}$, $^4M_{17/2}$	22701				17199
	22497	Emission	24236		17170
	22099	$^5D_3\rightarrow^7F_6$	24177		17111
$^4I_{13/2}$	21574		24026		17047
$^4I_{9/2}$	21119				17018
	20811		23009		16983
	20470	$^5D_3\rightarrow^7F_5$	22967		16897
$^4G_{7/2}$	20000		22883		16852
$^4F_{3/2}$	18867		22831		
			22789	$^5D_4\rightarrow^7F_3$	16239
Emission			22665		16196
$^4G_{5/2}\rightarrow^6H_{5/2}$	17749				16123
	17724	$^5D_3\rightarrow^7F_4$	21987		16103
	17605		21929		16072
			21872		16046
$^4G_{5/2}\rightarrow^6H_{7/2}$	16750		21834		
	16666			$^5D_4\rightarrow^7F_2$	15571
	16567	$^5D_3\rightarrow^7F_3$	21312		15527
	16534		21168		15508
			21061		15489
$^4G_{5/2}\rightarrow^6H_{9/2}$	15523		21034		15375
	15484				15323
	15417	$^5D_3\rightarrow^7F_2$	20798		15234
	15370		20755		
	15328		20721	$^5D_4\rightarrow^7F_1$	14992
					14929
$^4G_{5/2}\rightarrow^6H_{11/2}$	14196	$^5D_4\rightarrow^7F_6$	20508		14912
	14164		20458		
	14120		20408	$^5D_4\rightarrow^7F_0$	14766
	14076		20366		14710
	14048		20259		
	13989				

The experimental intensity parameters (η_{Sm}) of the $Gd_2(WO_4)_3$:Sm^{3+} system were determined and compared with those obtained for the Sm-complexes,[24] where η_{Sm} is the ratio between the intensities of the $^4G_{5/2}\rightarrow^6H_{9/2}$ and $^4G_{5/2}\rightarrow^6H_{5/2}$ transitions (Table 3). The $^4G_{5/2}\rightarrow^6H_{5/2}$ transition is taken as the reference due to its predominant magnetic dipole character. On the other hand, the hypersensitive $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition is forbidden by magnetic-dipole and allowed by forced electric-dipole. Additionally, the η_{Sm} values were compared to the experimental intensity parameter η_{Eu} for the $Gd_2(WO_4)_3$:Eu^{3+} compound prepared by both methods,[6,14] where the η_{Eu} parameter is the ratio between the area under the curves of the hypersensitive transition $^5D_0\rightarrow^7F_2$ allowed by forced electric-dipole and the $^5D_0\rightarrow^7F_1$ transition allowed by magnetic-dipole. The η_{Sm} values for the $Gd_2(WO_4)_3$:Sm^{3+} compound obtained by the Pechini ($\eta_{Sm} = 9.60$) and ceramic method ($\eta_{Sm} = 9.81$) are very close indicating that the Sm^{3+} ion is in a similar polarizable chemical environment in both Sm^{3+} compounds. Besides, it was observed a correlation between the values of η_{Sm} and η_{Eu} suggesting that the Sm^{3+} ion is in a similar polarizable environment and that the covalent character of the metal-donor atom interaction is also similar for these ions. Comparing the values of the η_{Sm} and η_{Eu}

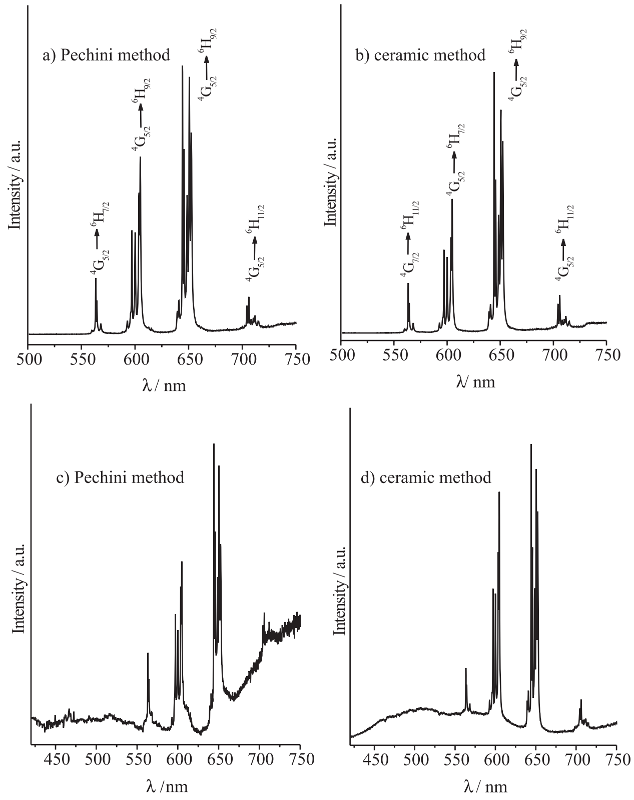

Figure 2. Emission spectra of the $Gd_2(WO_4)_3:Sm^{3+}$ compound recorded at 77 K prepared by Pechini method with excitation monitored at (a) 404 nm and (c) 265 nm and ceramic method under excitation at (b) 404 nm and (d) 265 nm.

parameters with those for other RE^{3+}-complexes it is observed that the chemical environment around the rare earth ions in the tungstate systems is less polarizable than in the $[RE(TTA)_3(PTSO)_2]$ complex.[24]

Table 3. Experimental intensity parameters for the $Gd_2(WO_4)_3:RE^{3+}$ systems and $[RE(TTA)_3(PTSO)_2]$ complexes (RE^{3+} = Sm and Eu)

Compound	η_{Sm}	η_{Eu}
$[RE(TTA)_3(PTSO)_2]^a$	13.37	20.85
$Gd_2(WO_4)_3:RE^{3+}$(ceramic method)	9.81	10.13
$Gd_2(WO_4)_3:RE^{3+}$(Pechini method)	9.60	9.84

[a] TTA = thenoyltrifluoroacetonate and PTSO = p-tolyl sulfoxide.[24]

In the present investigation, the excitation spectra of the $Gd_2(WO_4)_3:Tb^{3+}$ system prepared by the Pechini and ceramic methods were also obtained at 77 K in the spectral range from 250 to 520 nm, under emission at 544 nm (Figure 3). The spectrum of the Tb^{3+}-doped tungstate (Figure 3a) prepared by the Pechini method displays two broad bands around 290 and 370 nm attributed to ($O\rightarrow W^I$) and ($O\rightarrow W^{II}$) LMCT, respectively. On the other hand, the spectrum of the sample prepared by ceramic method (Figure 3b) shows two broad high intensity bands in the range 250-320 nm with maxima at 265 and 290 nm attributed to $O\rightarrow W^I$ LMCT state and $4f^8\rightarrow 5f^75d$ transitions from the terbium ion, respectively. The later transition (at around 320 nm) in Figure 3a is overlapped with the broad band arising from LMCT state. The excitation spectrum (Figure 3a) presents narrow bands arising from the $^7F_6\rightarrow{}^{2S+1}L_J$ transitions of Tb^{3+} ions (Table 2), which are overlapped with that broad band around 350 nm. As it can be seen, the narrow bands from the 4f-4f transitions of the rare earth ion (Figure 3b) are more defined for the system prepared by the ceramic method than for the Pechini one.

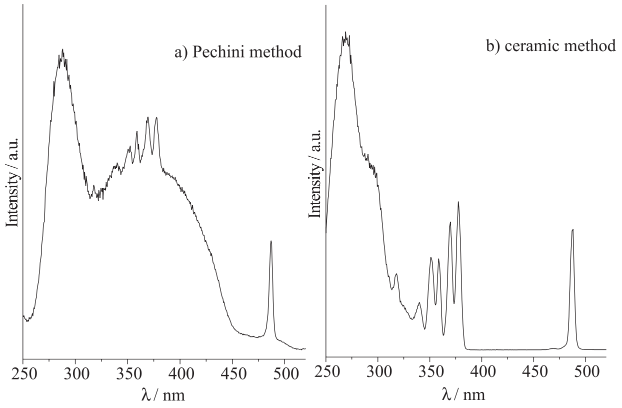

Figure 3. Excitation spectra of the $Gd_2(WO_4)_3:Tb^{3+}$ compound with emission monitored at 544 nm at liquid nitrogen temperature prepared by methods a) Pechini (750 °C) and b) ceramic (900 °C).

Figure 4a shows the emission spectrum of the $Gd_2(WO_4)_3:Tb^{3+}$ system prepared by the ceramic method, under excitation in the $^7F_6\rightarrow{}^5G_6$ transition (at 378 nm). This spectrum exhibits sharp emission bands, in the spectral range from 485 to 720 nm, which are attributed to the intraconfigurational $^5D_4\rightarrow{}^7F_J$ transitions (where J = 0-6). Additionally, the emission spectrum of the $Gd_2(WO_4)_3:Tb^{3+}$ system (Figure 4a) presents, in the interval between 400 and 475 nm, a series of weak bands originated from the $^5D_3$ excited level to the ^7F_J, where J= 2, 3, 4, 5 and 6 (Table 2). The emission spectra of the $Gd_2(WO_4)_3:Tb^{3+}$ system prepared by the Pechini method (figure not shown), under excitation at 378 nm, present similar spectral profile to that from the ceramic method (Figure 4a), exhibiting emission bands arising from both emitting $^5D_3$ and $^5D_4$ levels.

It is interesting to observe that the $^5D_3\rightarrow{}^7F_J$ transitions are not exhibited in the emission spectrum of the $Tb(WO_4)_3$ system (Figure 4b). Thus, in order to explain the presence of the bands arising from the $^5D_3\rightarrow{}^7F_J$ transitions in the spectra of the Tb-doped systems, it is made a comparative study between the emission spectrum of the undoped, $Tb_2(WO_4)_3$, and Tb-doped compounds prepared by the

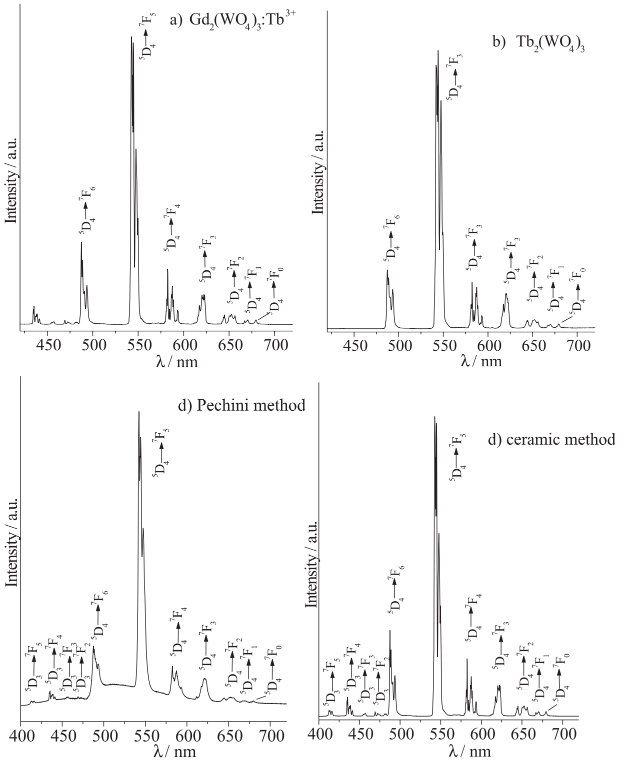

Figure 4. Emission spectra of the Tb^{3+}-compounds prepared by the ceramic method (900 °C), recorded at 77K, with excitation monitored at 378 nm a) $Gd_2(WO_4)_3$:Tb^{3+} and b) $Tb_2(WO_4)_3$. Emission spectra of the $Gd_2(WO_4)_3$:Tb^{3+} compound with excitation monitored at 265 nm at liquid nitrogen temperature prepared by methods c) Pechini (750 °C) and d) ceramic (900 °C).

ceramic method at 900 °C (Figures 4a and 4b). It is interesting to report that the spectrum of the compound that has highest concentration of the Tb^{3+} ions there are no narrow bands arising from the emitting $^5D_3$ level. These results indicate that the non-radiative decay from the $^5D_3$ to the $^5D_4$ state via cross-relaxation process plays an important role in the deactivation in the $^5D_3$ emitting state, which can be explained on the basis of the luminescence quenching and the energy gaps between the emitting $^5D_3$ - $^5D_4$ levels and $^7F_6$ - $^7F_0$ levels.[25,26]

It is interesting to notice that the $Gd_2(WO_4)_3$:Tb^{3+} system prepared by the Pechini method when excited in the O→W LMCT transition (around 270 nm) presents the bands arising from $^5D_{3,4} \rightarrow {}^7F_J$ (J = 0-6) transitions and a broad band with maximum at about 500 nm (Figure 4c). On the other hand, the emission spectrum of this system prepared by the ceramic method (Figure 4d) exhibits only those sharp bands assigned to the $^5D_{3,4} \rightarrow {}^7F_J$ transitions of the Tb^{3+} ion. This suggests that the energy transfer from the tungstate group to the rare earth ion is more efficient for the doped system prepared by ceramic method.

Conclusions

The $Gd_2(WO_4)_3$:RE^{3+} (RE = Sm and Tb) systems prepared by the Pechini method present average crystallite sizes approximately twice smaller than those prepared *via* the ceramic method. The excitation spectra of the same systems present different broad bands assigned to the O→W LMCT state. These results could be used as an advantageous tool when a different excitation wavelength is required in the production of a new efficient emission from the Sm^{3+} and Tb^{3+}- doped tungstate phosphors, since the Pechini method allows the preparation of the compound at reduced temperatures in contrast to the conventional method (ceramic). The experimental intensity parameters (η_{Sm}) show the similar hypersensitive character of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition in the Sm^{3+}-compound prepared by both methods. The presence of the transitions arising from emitting $^5D_3$ level of the doped system, $Gd_2(WO_4)_3$:Tb^{3+}, which are absent in the undoped compound [$Tb_2(WO_4)_3$], suggest that the cross-relaxation process is operative when the Tb^{3+} concentration is increased.

Acknowledgements

We thank the Brazilian agencies FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) and CNPq/RENAMI (Conselho Nacional de Desenvolvimento Científico e Tecnológico/Molecular and Interfaces Nanotechnology Research Network) for financial support.

References

1. Strek, W.; Bednarkiewicz, A.; Derén, P.J.; *J. Lumin.* **2001**, *92*, 229.
2. Nosenko, A.; Kostyk, L.; Koslovs'ka, L.; *J. Lumin.* **2000**, *90*, 49.
3. Do, Y.R.; Huh, Y.D.; *J. Electrochem. Soc*. **2000**, *147*, 4385.
4. Shi, F.; Meng, J.; Ren, Y.; Su, Q.; *J. Phys. Chem. Solids* **1998**, *59*, 105.
5. Makalik, L.; Hanuza, J.; Makalik, B.; Strek, W.; Legendziewicz, J.; *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 397.
6. Huang, J.; Loriers, J.; Porcher, P.; *J. Solid State Chem*. **1983**, *48*, 333.
7. MacDonald, R.E.; Vogel, M.J.; Brookman, J.W.; *IBM J. Res. Develop*. **1962**, *6*, 363.
8. Borchardt, H.J.; *J. Chem. Phys*. **1963**, *39*, 504.
9. Templeton, D.H.; Zalkin, A.; *Acta Cryst*. **1963**, *16*, 762.
10. Safari, A.; Lee, Y.H.; Halliyal, A.; Newnham, R.E.; *Am. Ceram. Soc. Bull.* **1987**, *66*, 668.

11. Paris, E.C.; Leite, E.R.; Longo, E.; Varela, J.A.; *Mater. Lett.* **1998**, *37*, 1.
12. Millar, C.E.; Pedersen, L.; Wolny, W.W.; *Ferroelectrics* **1992**, *133*, 271.
13. Kodaira, C.A.; Brito, H.F.; Malta, O.L.; Serra, O.A.; *J. Lumin*. **2003**, *101*, 11.
14. Kodaira, C.A.; Brito, H.F.; Felinto, M.C.F.C.; *J. Solid State Chem*. **2003**, *171*, 401.
15. Rambabu, U.; Khanna, P.K.; Buddhudu, S.; *Mater. Lett*. **1999**, *38*, 121.
16. Reisfeld, R.; Gaft, M.; Saridarov, T.; Panczer, G.; Zelner, M.; *Mater. Letters* **2000**, *45*, 154.
17. May, P.S.; Metcalf, D.H.; Richardson, F.S.; Carter, R.C.; Miller, C.E.; Palmer, R.A.; *J. Lumin*. **1992**, *51*, 249.
18. Beaury, L.; Hölsa, J.; Korventausta, J.; Krupa, J.C.; Lamminnäki, R.J.; Porcher, P.; Rahiala, H.; Säilynoja, P.E.; *Acta Phys. Polonica* A **1997**, *90*, 1203.
19. Binnemans, K.; Görller-Walrand, C.; *Chem. Phys. Lett*. **1995**, *235*, 163.
20. Amosov, V.M.; Plyushchev, V.E.; *Russ. J. Inorg. Chem.* **1967**, *2(5)*, 595.
21. Nassau, K.; Levinstein, H.; Loiacono, G. M.; *J. Phys. Chem. Solids* **1965**, *26*, 1805.
22. Burcham, L.J.; Wachs, I.E.; *Spectrochim. Acta Part A* **1998**, *54*, 1355.
23. Santilli, C.V.; Pulcinelli, S.H.; Brito, G.E.S.; Briois, V.; *J. Phys. Chem. B* **1999**, *103*, 2660.
24. Brito, H.F.; Malta, O.L.; Felinto, M. C. F. C.; Teotonio, E.E.S.; Menezes, J.F.S.; Silva, C.F.B.; Tomiyama, C.S.; Carvalho, C.A.A.; *J. Alloys Comp*. **2002**, *344*, 293.
25. Berdowski, P.A.M.; Lammers, M.J.J.; Blasse, G.; *Chem. Phys. Lett.* **1985**, *113*, 387.
26. Wakefield, G.; Keron, H.A.; Dobson, P.J.; Hutchison, J.L.; *J. Phys. Chem. Solids* **1999**, *60*, 503.

Received: February 17, 2004
Published on the web: November 5, 2004

FAPESP helped in meeting the publication costs of this article.