LUMINESCENCE PROPERTIES OF EUROPIUM AND TERBIUM ACTIVATED YTTRIUM NIOBIUM/TANTALATE PHOSPHORS UNDER VUV-UV EXCITATION

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(Received 18 August 2008)

Abstract

Various compositions of $Y(Ta,Nb)O_4:Eu^{3+},Tb^{3+}$ with different Nb and activator concentrations have been investigated under UV and VUV excitation. Some compounds with very strong emission under VUV excitation were found. Such phosphors could be proposed as very good emissive materials for Displays and Lightings.

1. Introduction

The growing interest in luminescence spectroscopy of rare earth ions in the vacuum ultraviolet (VUV) and the visible (VIS) spectral range is due to industrial demands for new applications. $YTaO_4$ and $YNbO_4$ phosphors are a perspective class of efficient materials that are generally used in X-ray intensifying screens. These phosphors exhibit satisfying luminescence whenever excited by UV light, cathode radiation or X ray. However, to our knowledge, no work has been published on the VUV-excited luminescence for Eu^{3+} and Tb^{3+} double activated yttrium niobate and yttrium tantalate based phosphors.

In this paper, the VUV–UV PL and PLE spectra of Eu^{3+} and/or Tb^{3+} ion activated yttrium niobium/tantalate phosphors are reported.

2. Experimental

Eu^{3+} and Tb^{3+} activated yttrium tantalate, yttrium niobium-tantalate, and yttrium niobate phosphors were prepared by solid state reaction from homogeneous mixture consisting of Y_2O_3, Eu_2O_3, Tb_4O_7, Ta_2O_5, Nb_2O_5, and Na_2SO_4 as flux. The powders mixture was fired in air at 1200°C, for 4 h and slowly cooled to the room temperature.

General formula of phosphors is $Y_{1-x-y}\ Eu_xTb_yTa_{1-z}Nb_zO_4$, where: $x + y = 0.05$ and $z = 0$; 0.15 and 1.00. The phosphor compositions of prepared samples are presented in Table 1.

Sample characterization was performed by X-ray diffraction (Rigaku X-ray Diffractometer). UV measurements were monitored using the Perkin-Elmer LS50B spectrometer with a xenon flash lamp. VUV excitation spectra of samples were measured using a VUV spectrophotometer equipped with VUV monochromator (ARC, VM 502) and a light source of 30W deuterium lamp (ARC, DS775-100).

Table 1. Composition of yttrium niobium/tantalate phosphors activated with Tb^{3+} and/or Eu^{3+}.

N	Phosphor type	Phosphor formula	Host lattice (mol%)		RE-activator (mol%)	
			$YTaO_4$	$YNbO_4$	Eu^{3+}	Tb^{3+}
1	$YTaO_4$	$YTaO_4$	100	-	-	-
2	$YTaO_4$:Eu	$Y_{0.95}Eu_{0.05}TaO_4$	100	-	5	0
3	$YTaO_4$:Eu,Tb	$Y_{0.95}Eu_{0.025}Tb_{0.025}TaO_4$	100	-	2,5	2,5
4	$YTaO_4$:Tb	$Y_{0.95}Tb_{0.05}TaO_4$	100	-	-	5
5	Y(TaNb)O_4	$YTa_{0.85}Nb_{0.15}O_4$	85	15	-	-
6	Y(TaNb)O_4:Eu	$Y_{0.95}Eu_{0.05}Ta_{0.85}Nb_{0.15}O_4$	85	15	5	-
7	Y(TaNb)O_4:Eu,Tb	$Y_{0.95}Eu_{0.025}Tb_{0.025}Ta_{0.85}Nb_{0.15}O_4$	85	15	2,5	2,5
8	Y(TaNb)O_4:Tb	$Y_{0.95}Tb_{0.05}Ta_{0.85}Nb_{0.15}O_4$	85	15	-	5
9	$YNbO_4$	$YNbO_4$	-	100	-	-
10	$YNbO_4$:Eu	$Y_{0.95}Eu_{0.05}NbO_4$	-	100	5	-
11	$YNbO_4$:Eu,Tb	$Y_{0.95}Eu_{0.025}Tb_{0.025}NbO_4$	-	100	2,5	2,5
12	$YNbO_4$:Tb	$Y_{0.95}Tb_{0.05}NbO_4$	-	100	-	5

3. Results and discussion

In Fig. 1, one can see the excitation spectra from some samples with different host lattices and different activators. The spectra were measured in the range from 100 to 350 nm using sodium salicylate powder as a reference. The excitation spectra were obtained by observing all emission light and calibrated by that of sodium salicylate, which has a constant quantum efficiency in the 115–300 nm range.

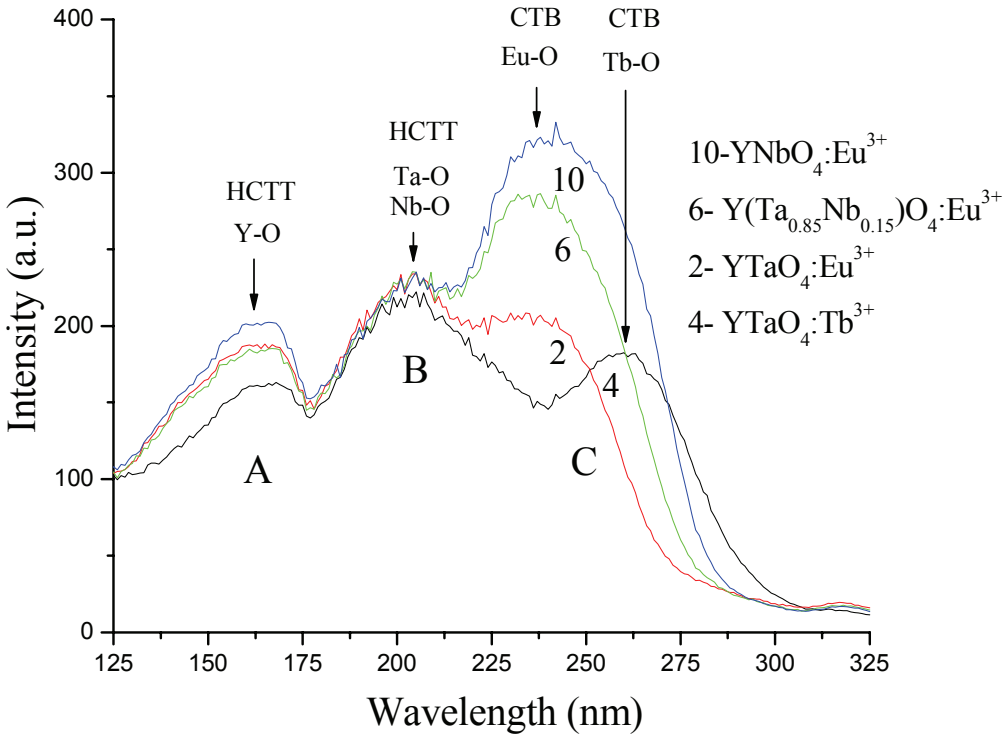

Fig. 1. Excitation spectra Y(Ta,Nb)O_4:Eu,Tb.

The numbers of the curves in Fig. 1 correspond to the numbers of samples in Table 1. It is clearly seen from Fig. 1 that all the samples have three obvious large bands A, B, and C in the VUV PLE spectra. About the VUV PLE spectra of rare earth ion activated luminescent materials five physical processes have been reported: (1) f–f transition of the rare earth ions; (2) f–d transition of the rare earth ions; (3) charge transfer band (CTB) from coordination anions to the rare earth ions; (4) the absorption of the host lattice; (5) electronic excitation of the host: high-energy photons of VUV excitation are absorbed in conduction band of the sample creating charge carriers like free electrons in conduction band and holes in valence band. In other words, excitation in the VUV range produces electron–hole pairs that undergo recombination at activator ions.

We believe that the three bands observed in the VUV range in $Y(Ta,Nb)O_4$:Eu,Tb are related to the following processes. It is no doubt that the band C with a maximum at 240 nm for Eu^{3+} (10, 6, 2) and 260 nm for Tb^{3+} (4) are the CTB of $O^{2-} \rightarrow Eu^{3+}$ or $O^{2-} \rightarrow Tb^{3+}$ in $Y(Ta,Nb)O_4$ host lattices. Namely, the electron delocalized from the filled 2p shell of O^{2-} to the partially filled 4f shell of Eu^{3+} or Tb^{3+}. For sample N3, for example (Fig. 2), when the two activators Eu^{3+} and Tb^{3+} are introduced together in equal concentration (2.5 mol %), the peak position of this CTB is observed at 250 nm, exactly between 240 and 260 nm.

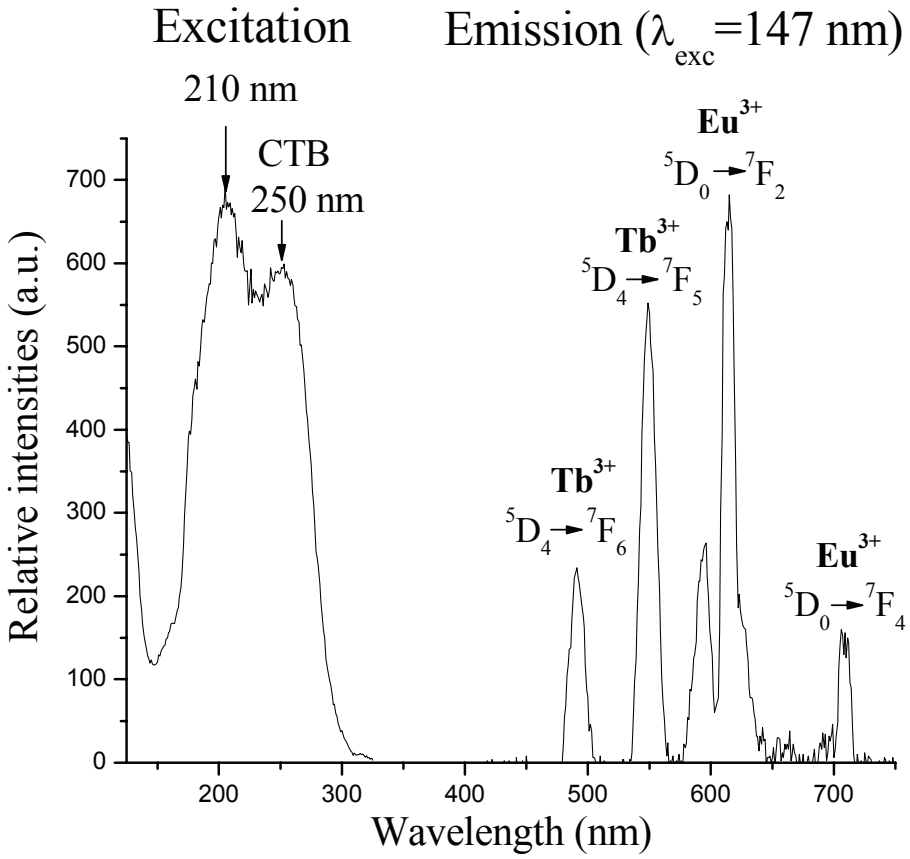

Fig. 2. The emission and excitation spectra from $YTaO_4:Eu^{3+},Tb^{3+}$.

The contribution of Eu^{3+} and Tb^{3+} in emission process under VUV excitation is clearly seen in Fig. 2. Moreover, the strong Eu^{3+} emission of $^5D_0 \rightarrow {}^7F_4$ transition appears. Usually, this emission is very weak and could not be seen under UV excitation. The detailed branching ratio of $^5D_0 \rightarrow {}^7F_j$ transitions is presented in Table 2.

Table 2. Branching ratio of $^5D_0 \rightarrow ^7F_j$ transitions (Eu^{3+} concentration = 5 mol %).

Transitions	$YtaO_4:Eu^{3+}$		$Yta_{0.85}Nb_{0.15}O_4:Eu^{3+}$		$YnbO_4:Eu^{3+}$	
	λ_{exc}=254nm	λ_{exc}=147nm	λ_{exc}=254nm	λ_{exc}=147nm	λ_{exc}=254nm	λ_{exc}=147nm
$^5D_0 \rightarrow ^7F_1$	48	30	39	26	25	13
$^5D_0 \rightarrow ^7F_2$	100	100	100	100	100	100
$^5D_0 \rightarrow ^7F_4$	1.3	25	1.4	22	1.1	13

Comparing UV (254 nm) and VUV (147 nm) excitation, we found in different investigated host lattices that the relative intensity of $^5D_0 \rightarrow ^7F_j$ main emission peaks, so called branch ratio, varies with not only the europium activation but also with the excitation wavelength. Under UV excitation the $^5D_0 \rightarrow ^7F_4$ emission is mostly trapped by the empty upper levels. In contrast, it is more likely that such empty levels can be readily filled under VUV excitation. This model explains the appearance of visible $^5D_0 \rightarrow ^7F_4$ transition and the increment of the luminescence intensity under VUV excitation.

The band B (Fig. 1) from 180 to 220 nm does not depend on the activator and it is almost the same for $YtaO_4$ and $YnbO_4$. We associate it with the absorption of the host lattices. The TaO_4^{3-} and NbO_4^{3-}groups can absorb excitation energy through $O^{2-} \rightarrow Ta^{5+}$ charge transfer transition or $O^{2-} \rightarrow Nb^{5+}$ and can transfer the energy to rare-earth luminescent centers, which give rise to the corresponding characteristic emission. The typical excitation and emission of TaO_4^{3-} group in $YtaO_4$ are shown in Fig. 3.

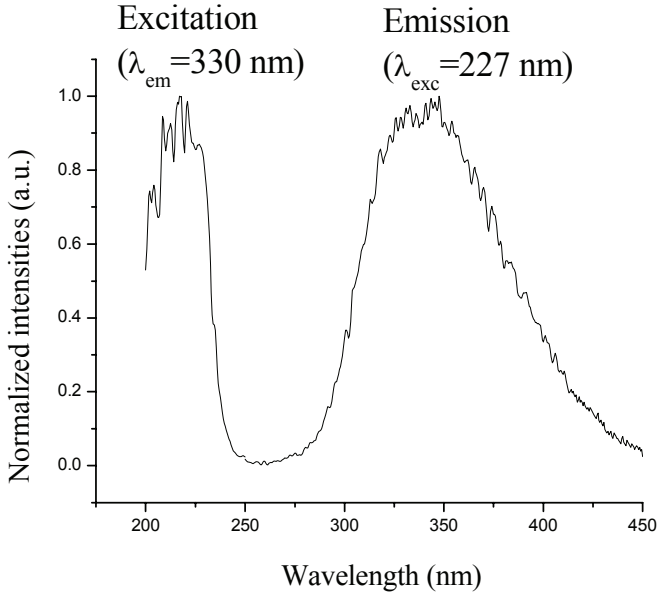

Fig. 3. The emission and excitation spectra from $YtaO_4$.

Since the absorption in $YtaO_4$ in comparison with $YnbO_4$ is shifted to the short wavelength region, this material cannot be excited by 254 nm, and higher energy excitation like X-ray, cathodoluminescence, or VUV should be applied.

The band A, peaked around 160 nm, is probably related to the host absorption. The Y-O bonds are excited and the energy is transferred to activators. Since Eu^{3+} and Tb^{3+} substitute Y^{3+} in the host lattice, the charge transfer between Eu^{3+} as well as Tb^{3+} and O^{2-} is also possible. The position of this band A for Y^{3+}, Eu^{3+} and Tb^{3+} ions can be calculated with the help of an empirical formula given by Jorgensen [1]

$$E_{CT} = [(X)-(M)] \times 30,000 \text{ cm}^{-1}$$

Here E_{CT} gives the position of the CTB in cm^{-1}, (X) the optical electronegativity of the anion, and (M) that of the central metal ion. Using Pauling scale for electronegativity [2], namely, (O)=3.44, (Y)=1.22, (Eu)=1.20, and (Tb)=1.10, the CTB of Y-O, Eu-O, and Tb-O can be estimated near 67,000 cm^{-1}, or around 150-160 nm. The results are close to the O^{2-} - Tb^{3+} CT bands 68,100 cm^{-1} (RE=Y) and 63,500 cm^{-1} (RE=La) reported by I.Gerard et al. [3].

One more advantage of VUV investigation is illustrated in the Fig. 4. For monoclinic M'-type crystalline structure, to which $YtaO_4:Tb^{3+}$ belongs, C_2 symmetry is demonstrated. From selection rules all transitions $^5D_4$-^7F_j for Tb^{3+} are allowed. But under UV excitation (254 nm) only some most intensive transitions can be observed. At 147 nm all of them can be seen.

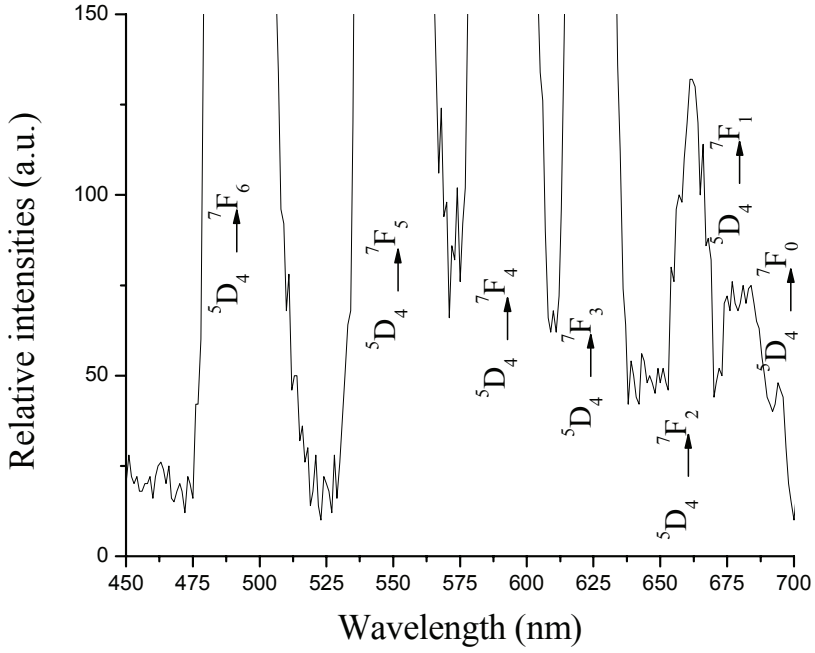

Fig. 4. The fragment of emission spectra from $YtaO_4:Tb^{3+}$.

4. Conclusions

$Y(Ta,Nb)O_4:Eu^{3+},Tb^{3+}$ phosphors with good luminescent properties under VUV excitation could be proposed as available emissive materials for Displays and Lightings.

References

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