

Spectral investigations on niobium and rare earth activated yttrium tantalate powders

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Europium and/or terbium 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. Photoluminescence spectroscopy, X-ray diffraction and FTIR spectroscopy were used to investigate the structural and luminescent properties of $Y(Ta,Nb)O_4$: Eu/Tb phosphors. Phosphor powders with variable photoluminescence colours from blue-to-green-to-yellow-to-red were obtained by thermal synthesis. Emission spectra enabled us to put in evidence the energy transfer from the tantalate/niobate host lattice to the rare earth emission centres. A mutual interaction between europium and terbium could be also considered.

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1. Introduction

Europium and/or terbium activated yttrium tantalate, yttrium niobium-tantalate and yttrium niobate powders, $Y(Ta,Nb)O_4$: Eu/Tb are of great interest from both scientific and application point of view. In these phosphors, host-lattice emission centers and rare earth emission centers can both contribute to the overall luminescence. Due to their variable luminescence chromaticity, rare earth activated yttrium tantalate-type phosphors are promising materials for optoelectronics.

Yttrium niobium-tantalate, $Y(Ta,Nb)O_4$ is an efficient blue-emitting luminescent material used in X-ray medical imaging [1,2]. Performances of $Y(Ta,Nb)O_4$ phosphors are correlated with composition and crystalline structure, particle dimensions and luminescence properties of powders. It is known that, depending on the synthesis conditions, $YTaO_4$ -based phosphors can present different crystalline structures; their high luminescence performances are correlated with the monoclinic crystalline structure representing the equilibrium phase at room temperature [3-7].

In $Y(Ta,Nb)O_4$ phosphors, the blue-light emission is associated with TaO_4 and NbO_4 groups from the host crystalline lattice. Luminescent emission could be shifted toward longer wavelengths when rare earth ions such as Eu^{3+} or Tb^{3+} are used to partially replace the yttrium ions into the host crystalline lattice. In this case, Eu- or Tb-emission centers are created that can generate the specific red and green luminescence, respectively.

In order to obtain $YTaO_4$ type phosphors with variable luminescence chromaticity, some $Y(Ta,Nb)O_4$: Eu,Tb phosphor samples were prepared and characterised. The goal of the paper is to establish a correlation between the composition, the crystalline structure and the luminescent emission of phosphors and to put in evidence a possible interaction between the different emission centers.

2. Experimental part

Yttrium tantalate, yttrium niobium-tantalate and yttrium tantalate phosphors activated with europium and/or terbium, $Y(Ta,Nb)O_4$: Eu, Tb, were prepared by solid state reaction, from homogeneous mixtures consisting of Y_2O_3 (99.9%), Ta_2O_5 (Optipur) and Nb_2O_5 (99%) as oxide precursors for the host lattice, Eu_2O_3 and/or Tb_4O_7 as activator system and Na_2SO_4 (99 %) as flux. The stoichiometric amounts of Y_2O_3 , Ta_2O_5 and/or Nb_2O_5 , Eu_2O_3 and/or Tb_4O_7 together with 30 wt % alkaline sulphates were ball-milled with acetone and dried at 70°C. The reactive oxide-flux mixture was prepared in a planetary-mill (Pulverisette type; agate balls and mill-beaker set). The powders mixture was fired in air at 1200°C, for 4 h and slowly cooled to the room temperature. Finally, phosphors samples were water washed, dried and sieved.

Sample characterization was performed by *infrared absorption spectroscopy* (FTIR spectra; JASCO 610 FTIR Spectrometer; KBr pellets), *photoluminescence*

measurements (emission and excitation spectra; JASCO FP-6500 Spectrofluorimeter Wavel; Glass filter WG 320; internal standard of CaWO_4 phosphor) and *X-ray diffraction* (XRD-patterns; D8Advanced Brucker Diffractometer, $\text{CuK}\alpha$ radiation). The interpretation of XRD data was achieved on the basis of some powder diffraction files namely, PDF 0072-0045 for monoclinic $\text{M}'\text{-YTaO}_4$, PDF 0024-1415 for monoclinic M-YTaO_4 , PDF 00-048-0265 for orthorhombic- Y_3TaO_7 and PDF 0023-1486 for monoclinic M-YNbO_4 .

3. Results and discussion

Three types of luminescent materials were prepared namely rare earth activated yttrium tantalate, rare earth activated yttrium niobium-tantalate and rare earth activated yttrium niobate phosphor samples, $\text{Y}(\text{Ta},\text{Nb})\text{O}_4$: Eu, Tb. General formula of phosphors is $\text{Y}_{1-x-y}\text{Eu}_x\text{Tb}_y\text{Ta}_{1-z}\text{Nb}_z\text{O}_4$, where $x + y = 0.05$ and $z = 0; 0.15$ and 1.00 . The phosphor composition of the as prepared samples are presented in table 1.

The formation of $\text{Y}(\text{Ta},\text{Nb})\text{O}_4$: Eu, Tb phosphors could be described by the equation:

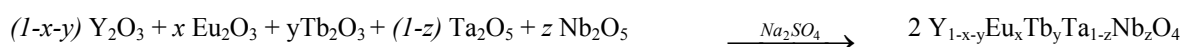


Table 1. Composition of yttrium tantalate –type phosphors activated with terbium and/or europium

Code	Phosphor type	Phosphor formula	Host lattice (mol%)		Re-activator (mol%)	
			YTaO ₄	YNbO ₄	Eu	Tb
IF-1	YTaO ₄	YTaO ₄	100	-	-	-
IF-2	YTaO ₄ :Eu	Y _{0.95} Eu _{0.05} TaO ₄	100	-	-	0
IF-3	YTaO ₄ :Eu,Tb	Y _{0.95} Eu _{0.025} Tb _{0.025} TaO ₄	100	-	2,5	2,5
IF-4	YTaO ₄ :Tb	Y _{0.95} Tb _{0.05} TaO ₄	100	-	-	5
IF-5	Y(TaNb)O ₄	YTa _{0.85} Nb _{0.15} O ₄	85	15	-	-
IF-6	Y(TaNb)O ₄ :Eu	Y _{0.95} Eu _{0.05} Ta _{0.85} Nb _{0.15} O ₄	85	15	5	-
IF-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
IF-8	Y(TaNb)O ₄ :Tb	Y _{0.95} Tb _{0.05} Ta _{0.85} Nb _{0.15} O ₄	85	15	-	5
IF-9	YNbO ₄	YNbO ₄	-	100	-	-
IF-10	YNbO ₄ :Eu	Y _{0.95} Eu _{0.05} NbO ₄	-	100	5	-
IF-11	YNbO ₄ :Eu,Tb	Y _{0.95} Eu _{0.025} Tb _{0.025} NbO ₄	-	100	2,5	2,5
IF-12	YNbO ₄ :Tb	Y _{0.95} Tb _{0.05} NbO ₄	-	100	-	5

XRD diffraction patterns illustrate the fact that all samples obtained in our synthesis conditions are monoclinic (Fig.1). YTaO_4 based phosphors are multiple-phase materials containing mainly the monoclinic M' type crystalline phase; additional diffraction lines (O) for orthorhombic Y_3TaO_7 can be noticed. The addition of the rare earth ions (terbium) does not ameliorate the basic structure, but increases the cell unit volume from 0.1441 to 0.1455 nm^3 . Instead, yttrium niobate sample is almost a single-phase material with the monoclinic M' - type crystalline structure. The addition of europium into the YNbO_4 also increases the cell unit volume from 0.1436 to 0.1440 nm^3 .

FT-IR spectra registered in the $1000\text{-}400 \text{ cm}^{-1}$ range, show a complex pattern, which could be interpreted according to a structure with more or less distorted TaO_6 units, which share edges with one another in the monoclinic modification of M' - type YTaO_4 (Fig. 2).

It is known that, in M' -type YTaO_4 , tantalum atoms are in distorted octahedron coordination (six Ta-O bonds),

whereas in monoclinic M -type YTaO_4 , tantalum atoms are in tetrahedral coordination (four Ta-O bonds)[4]. The shape of FT-IR spectra in the domain of MO_4 group vibrations (where $\text{M} = \text{Ta}, \text{Nb}$) illustrates the change of the metal-oxygen bonds number on measure that the niobium concentration increases. Yttrium niobate possesses monoclinic structure (similar to M-YTaO_4), with tetrahedral coordination of niobium.

The infrared spectra confirm that the crystalline arrangement of YTaO_4 , $\text{Y}(\text{Ta},\text{Nb})\text{O}_4$ YNbO_4 samples is different, as already suggested by the XRD patterns.

Photoluminescence measurements (Figs.3-4) put in evidence the change of luminescence chromaticity and sensitivity to UV excitation of YTaO_4 -samples when tantalum is partially replaced by niobium and yttrium is partially substituted with europium and/or terbium, respectively.

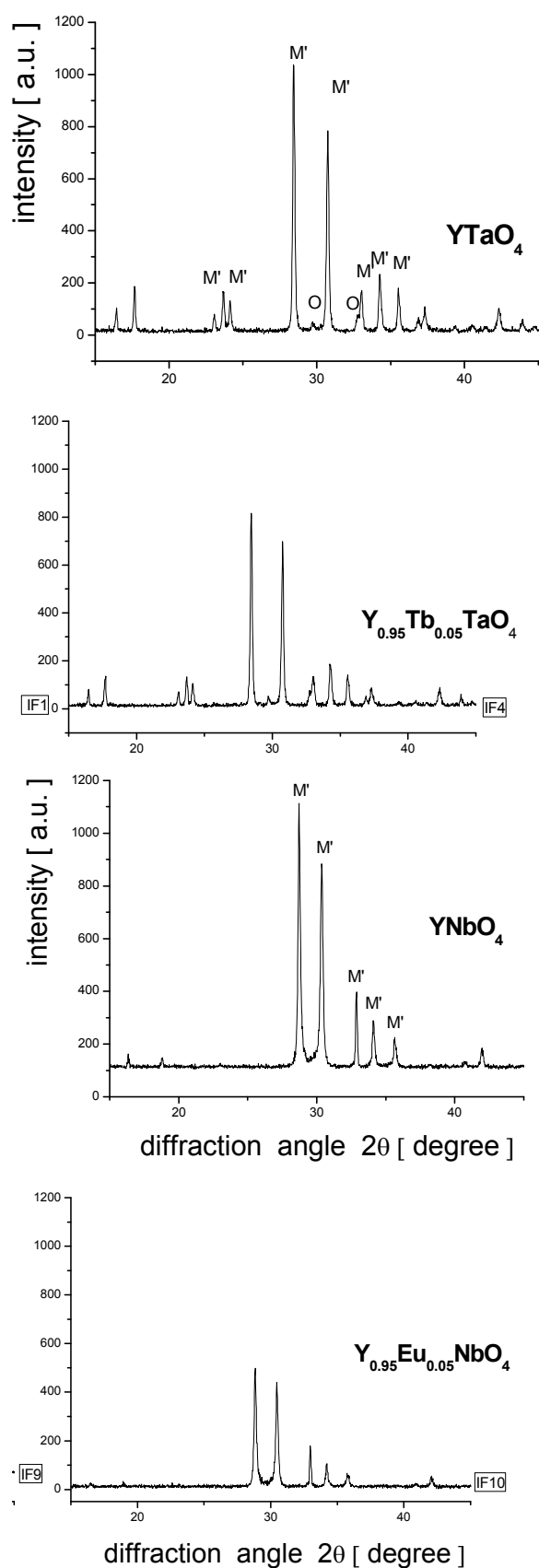


Fig. 1. XRD patterns of IF1 (YTbO_4), IF4 ($\text{Y}_{0.95}\text{Tb}_{0.05}\text{TaO}_4$), IF9 (YNbO_4) and IF10 ($\text{Y}_{0.95}\text{Eu}_{0.05}\text{NbO}_4$) samples prepared at 1200°C with Na_2SO_4 .

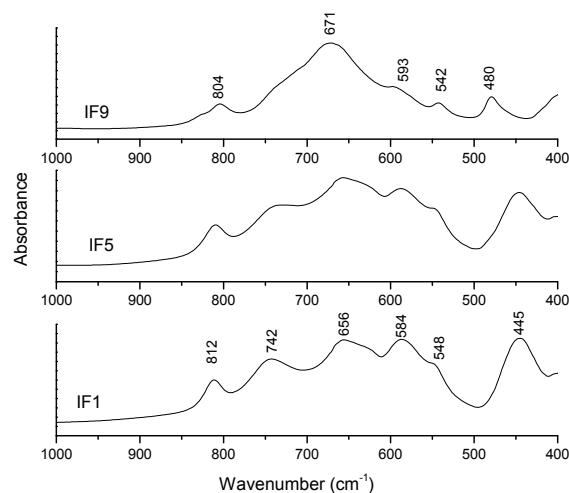


Fig. 2. FTIR spectra of IF1 (YTbO_4), IF5 ($\text{Ta}_{0.85}\text{Nb}_{0.15}\text{O}_4$) and IF9 (YNbO_4) phosphors prepared at 1200°C with Na_2SO_4 .

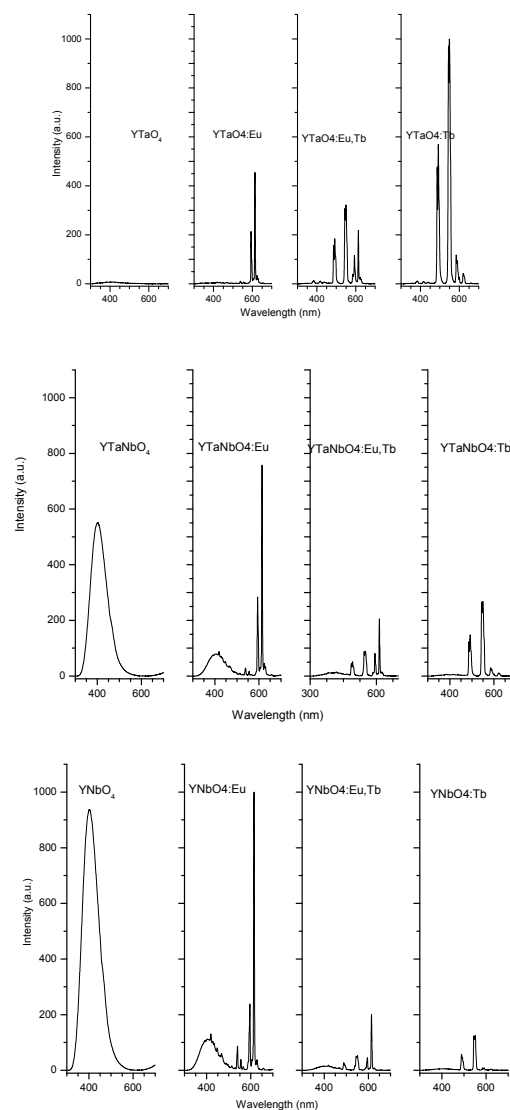


Fig. 3. Emission spectra of $\text{Y}_{1-x-y}\text{Eu}_x\text{Tb}_y\text{Ta}_{1-z}\text{Nb}_z\text{O}_4$ samples, $x + y = 0.05$; $0 \leq z \leq 1$ ($\lambda_{\text{exc}} = 254 \text{ nm}$).

Yttrium tantalate with no activators is practically not excited with 254 nm UV radiation. The photoluminescence centered at about 403 nm becomes much more strong when tantalum is partially or totally replaced by niobium. When rare earth ions such as Eu^{3+} and/or Tb^{3+} are used to substitute for yttrium ions into the YTaNbO_4 or YNbO_4 structure, the luminescence colour shifts toward longer wavelengths.

The luminescence of tantalate based phosphors is due to a charge transfer transition into the tantalate TaO_4 and/or NbO_4 group. Incorporation of the rare earth ions leads to the expected emission associated with the specific electronic transitions $^5\text{D}_4 \rightarrow ^7\text{F}_J$ for Tb^{3+} and $^5\text{D}_0 \rightarrow ^7\text{F}_J$ for Eu^{3+} ions. In our samples, the characteristic red emission band of europium is observed at ~ 614 nm while the specific green emission of terbium appears as bands at 544 and 549 nm.

Under 254 nm excitation, the best Eu-red emission appears in YNbO_4 matrix while the most intense Tb-green emission is observed in YTaNbO_4 matrix. The Eu-Tb simultaneous activation seems not to generate a very performing luminescent material. The double activation is most effective in YTaNbO_4 matrix.

Niobium addition into YTaNbO_4 : RE is in the favour of europium incorporation and consequently, to the formation of red-emission centres. On the contrary, incorporation of niobium does not facilitate the formation of terbium centres. In double activated samples, niobium addition seems to have no effect on europium emission. A very good energy transfer from the yttrium niobate lattice toward europium ions is observed.

Excitation spectra illustrate the sensitivity of yttrium tantalate based materials toward UV or visible radiation (Fig.4). For YTaNbO_4 matrix containing 5 mol% europium (IF2), the spectrum contains a strong excitation band at about 248 nm corresponding to the charge transfer from the host lattice toward Eu^{3+} ions and many relatively weak bands (320; 363; 383; 395; 466; 536 nm) corresponding to $^7\text{F}_J \rightarrow ^5\text{D}_0$ transitions inside the Eu^{3+} ions. As expected, the 614 nm band is less excited in the double activated material that contains only 2.5 mol% Eu (IF3) and almost not excited in samples with no europium (IF1; IF4).

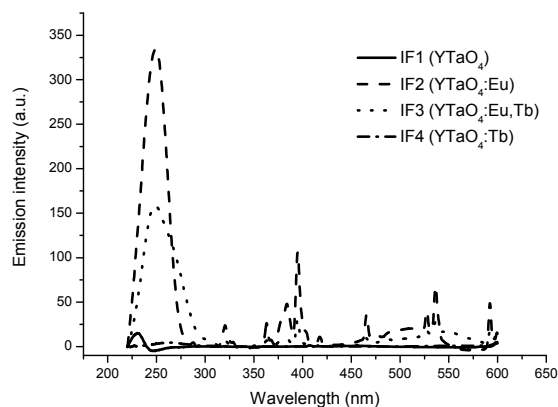


Fig. 4. Excitation spectra of some $\text{Y}_{1-x-y}\text{Eu}_x\text{Tb}_y\text{TaO}_4$ samples ($\lambda_{\text{em}} = 612$ nm)

4. Conclusions

In our working conditions, phosphor powders with variable luminescence colours from blue-to-green-to-yellow-to-red were obtained by doping monoclinic yttrium niobium and/or yttrium tantalate with europium and/or terbium. Emission and excitation spectra enabled us to put in evidence the energy transfer from the tantalate/niobate host lattice to the rare earth emission centres. A mutual interaction between europium and terbium could be also considered.

Acknowledgements

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